ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

DESIGN AND LIFE CYCLE ASSESSMENT OF INTEGRATED ORGANOSOLV BASED BIOREFINERY: SIMULATED CASE STUDIES UTILIZING SESSILE OAK (*Quercus petraea*) COPPICES AND INDUSTRIAL WOOD SAWDUST FROM BURSA/TURKEY REGION

Ph.D. THESIS

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Thesis Advisor: Prof. Dr. Filiz KARAOSMANOĞLU

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ENTEGRE ORGANOSOLV BAZLI BİYORAFİNERİ TASARIMI VE YAŞAM DÖNGÜSÜ DEĞERLENDİRMESİ: BURSA/ TÜRKİYE BÖLGESİNDEN SAPSIZ MEŞE (*Quercus petraea*) VE ENDÜSTRİYEL ODUN TALAŞI KULLANARAK DURUM ÇALIŞMALARI SİMÜLASYONU

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HAZİRAN 2019

Merve Nazlı BORAND, a Ph.D. student of ITU Graduate School of Science Engineering and Technology student ID 506112008, successfully defended the thesis entitled “Design and Life Cycle Assessment of Integrated Organosolv Based Biorefinery: Simulated Case Studies Utilizing Sessile Oak (*Quercus petraea*) Coppices and Industrial Wood Sawdust from Bursa/Turkey Region”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my lovely family,

FOREWORD

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April 2019 — Merve Nazlı BORAND

İstanbul — (Chemical Engineer, M.Sc.)

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ABBREVIATIONS

ABE : Acetone-Butanol-Ethanol
ADP : Abiotic Depletion Potential
AFEX : Ammonia Fiber Explosion
ALCA : Attributional Life Cycle Assessment
ALCI : Attributional Life Cycle Inventory
ALO : Agricultural Land Occupation
AMIMCl : 1-Allyl-3-Methylimidazolium Chloride
AP : Acidification Potential
ARP : Ammonia Recycle Percolation
ASPEN : Advanced System for Process Engineering
ASPENPCD : Aspen Plus Pure Component Databank
B85 : 85% Biodiesel and 15% Diesel Mixture
B95 : 95% Biodiesel and 5% Diesel Mixture
B100 : 100% Biodiesel
BDTACl : Benzyl Dimethyl Tetradecyl Ammonium Chloride
BMIMCl : 1-N-Butyl-3-Methylimidazolium Chloride
C5 : Five Carbon Sugars
C6 : Six Carbon Sugars
C9 : 9 Carbon Units
CC : Climate Change
CHP : Combined Heat and Power
CLCA : Consequential Life Cycle Assessment
CLCI : Consequential Life Cycle Inventory
CSL : Corn Steep Liquor
CSTR : Continuous Stirred Tank Reactor
CS-1 : Case Study 1
CS-2 : Case Study 2
CS-3 : Case Study 3
DALY : Disability Adjusted Life Years

DAP : Diammonium Phosphate

DQI : Data Quality Indicators

E5 : 5% Bioethanol and 95% Gasoline Mixture

E10 : 10% Bioethanol and 90% Gasoline Mixture

E25 : 25% Bioethanol and 75% Gasoline Mixture

E70 : 70% Bioethanol and 30% Gasoline Mixture

E85 : 85% Bioethanol and 15% Gasoline Mixture

E95 : 95% Bioethanol and 5% Gasoline Mixture

E100 : 100% Bioethanol

ENG : English Engineering

EP : Eutrophication Potential

EPA : Environmental Protection Agency

ETBE : Ethyl Tertiary Butyl Ether

EQ : Ecosystem Quality

EU : European Union

FD : Fossil Depletion

FE : Freshwater Eutrophication

FEC : Freshwater Ecotoxicity

FTS : Fischer-Tropsch Synthesis

GDF : General Directorate of Forestry

GHG : Greenhouse Gas

GLO : Global

GMA : Gasification and Mixed Alcohols

GWP : Global Warming Potential

HH : Human Health

HHV : Higher Heating Value

HMF : Hydroxy Methyl Furfural

HPLC : High-Performance Liquid Chromatography

HT : Human Toxicity

HTP : Human Toxicity Potential

ID : Identification

IEA : International Energy Agency

Ils : Ionic Liquids

IOBB : Integrated Organosolv Based Biorefinery

IPCC : International Intergovernmental Panel on Climate Change

IPP : Integrated Product Policy

IRENA : International Renewable Energy Agency

IR : Ionizing Radiation

ISO : International Organization for Standardization

IWS : Industrial Wood Sawdust

LCA : Life Cycle Assesment

LCF : Lignocellulosic Feedstock Biorefineries

LCI : Life Cycle Inventory

LCIA : Life Cycle Impact Assessment

LHW : Liquid Hot Water

MBPCl : 3-Methyl-N-Butylpyridinium Chloride

MD : Metal Depletion

MDF : Medium Density Fiberboard

ME : Marine Eutrophication

MEC : Marine Ecotoxicity

MET : Metric Engineering

MFRI : Marmara Forest Research Institute

MoFWA : The Ministry of Forestry and Water Affairs

MRI : Midwest Research Institute

MTBE : Methyl Tertiary Butyl Ether

MWI : Microwave Irradiation

NLT : Natural Land Transformation

NMMO : N-Methyl Morpholine-N-Oxide Monohydrate

NREL : National Renewable Energy Laboratories

NRTL : Non-Random Two-Liquid

NRTL-RK : Non-Random Two Liquids Redlich Kwong

OD : Ozone Depletion

ODP : Ozone Depletion Potential

PHB : Polyhydroxybutyrate

PMF : Particulate Matter Formation

PNNL : Pacific Northwest National Laboratory

POCP : Photochemical Ozone Creation Potential

POF : Photochemical Oxidant Formation

PSD : Particle Size Distribution

PV : Photovoltaic

REPA : Resource and Environmental Profile Analysis
RKS : Redlich-Kwong-Soave
ROW : Rest of the World
SETAC : The Society of Environmental Toxicology and Chemical
SHF : Saccharification and Fermentation using Acid Hydrolysis
SI : International System
SOC : Sessile Oak Coppice
SRC : Short Rotation Coppice
SRF : Short Rotation Forestry
SSCF : Simultaneous Saccharification and Co-Fermentation
SSF : Simultaneous Saccharification and Fermentation
TA : Terrestrial Acidification
TEC : Terrestrial Ecotoxicity
TOA : Trioctylamine
TOPO : Trioctyl Phosphine Oxide
TÜBİTAK : The Scientific and Technological Research Council of Turkey
ULO : Urban Land Occupation
UNEP : United Nations Environment Programme
UN WCED : United Nations World Commission on Environment and Development
USA : United States of America
US DOE : US Department of Energy
WD : Water Depletion
YÖK : Council of Higher Education

SYMBOLS

atm : Atmospheric Pressure
$\mathbf{C_4H_3OCHO}$: Furfural
$\mathbf{C_5H_7NO_2}$: Microbial Cell
$\mathbf{C_5H_8O_3}$: Levulinic Acid
$\mathbf{C_6H_6O_3}$: 5-Hydroxy Methyl Furfural
$\mathbf{C_8H_{17}OH}$: Octanol
$\mathbf{C_{11}H_{24}}$: Undecane
CFCs : Chlorofluorocarbons
$\mathbf{Ca(OH)_2}$: Calcium Hydroxide
$\mathbf{CCl_3CH_3}$: 1,1,1-Trichloroethane
$\mathbf{CCl_4}$: Tetrachloromethane
$\mathbf{CH_2O_2}$: Formic Acid
$\mathbf{CH_3Br}$: Methyl Bromide
$\mathbf{CH_3COOH}$: Acetic Acid
$\mathbf{CH_4}$: Methane
$\mathbf{Cl_2}$: Chlorine
$\mathbf{ClO_2}$: Chlorine Dioxide
CO : Carbon Monoxide
$\mathbf{CO_2}$: Carbon Dioxide
$\mathbf{CO_{2eq}}$: Carbon Dioxide Equivalent
GW : Gigawatt
GWh : Gigawatt-hour
$\mathbf{H_2}$: Hydrogen
$\mathbf{H_2O_2}$: Hydrogenperoxide
$\mathbf{H_2S}$: Hydrogen Sulfide
$\mathbf{H_2SO_4}$: Sulfuric Acid
$\mathbf{H_3PO_4}$: Phosphoric Acid
ha : Hectare
HCFCs : Hydrochlorofluorocarbons
HCl : Hydrogen Chloride

HF : Hydrogen Fluoride
HNO_3 : Nitric Acid
Kcal : Kilocalories
kg : Kilograms
KOH : Potassium Hydroxide
kW : Kilowatt
kWh : Kilowatt-hour
L : Liter
M : Molarity
MJ : Mega Joule
min : Minutes
ml : Milliliter
mm : Millimeter
MPa : Mega Pascal
Mtoe : Million Ton Oil Equivalent
MW : Megawatt
MWe : Megawatt Electrical
N : Normality
N_2O : Nitrous Oxide
NaClO : Sodium Hypochlorite
NaOH : Sodium Hydroxide
NH_4 : Ammonium
NMHC : Non-methane Hydrocarbon
NO : Nitrogen Monoxide
NO_x : Nitric Oxide
NO_2 : Nitrogen Dioxide
NH_4OH : Ammonium hydroxide
O_2 : Oxygen
O_3 : Ozone
PJ : Peta Joule
P_c : Critical Pressure
PO_4 : Phosphate
Pt : Point
SO_2 : Sulfur Dioxide
SO_x : Sulfur Oxides

t : Ton

T_c : Critical Temperature

toe : Ton Oil Equivalent

v : Volume

w : Weight

y : Year

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DESIGN AND LIFE CYCLE ASSESSMENT OF INTEGRATED ORGANOSOLV BASED BIOREFINERY: SIMULATED CASE STUDIES UTILIZING SESSILE OAK (*Quercus petraea*) COPPICES AND INDUSTRIAL WOOD SAWDUST FROM BURSA/TURKEY REGION

SUMMARY

The concept of biorefineries is similar to conventional fossil refineries except it uses biomass as a feedstock instead of fossil fuels. Biorefineries convert biomass to biofuel, biopower, biochemical and biomaterial via chemical and biological processes. The several classifications of biorefinery have accepted by authorities. Firstly, biorefineries classified into feedstock/process/product specialties. First generation biorefineries use one feedstock in one process and produce one product. Second generation biorefineries convert one feedstock in multiple processes and produce more than one product. Third generation biorefineries use various feedstocks in different processes and produce several products. The other classification based on the feedstock of biorefineries. In this classification contains lignocellulosic feedstock biorefinery (LCF), whole crop biorefinery, green biorefineries, marine biorefinery, and the biorefinery two platforms concept. Lignocellulosic feedstock biorefineries convert lignocellulosic biomass for producing biofuels, biopower, biochemicals, and biomaterials. Lignocellulosic biomass covers both woody and non-woody biomass which includes mainly polymeric glucan (cellulose), polymeric other sugars (hemicellulose), and lignin.

According to the recalcitrant structure of lignocellulosic biomass, pretreatment methods have to apply to separate lignin from hemicellulose and cellulose fraction. Additionally, pretreatment methods decrease the crystalline structure of cellulose, improve the biomass surface area, prevents the inhibitor production during hydrolysis and fermentation, decrease the cost of the process and reduce the consumption of conventional energy. The general classification of pretreatment methods is physical pretreatment, physicochemical pretreatments, biological pretreatments, and chemical pretreatments. Organosolv pretreatment is one of the most promising delignification methods for lignocellulosic biomass. The main difference of organosolv pretreatment is obtaining lignin nearly pure form, although lignin is a waste product for other pretreatment methods. Therefore, lignin is produced as a high-value chemical and used as a feedstock for chemical production. Organosolv pretreatment is a simultaneous delignification method in existence with organic solvents and acidic or basic catalysts.

The technical potential for biomass in Turkey is crucial. Although the biomass usage in modern technology has not been developed until recently and used mostly in conventional combustion, the importance of biomass is appreciated. Modern forestry provides the biomass application in biorefineries. The oak coppice forests, both unproductive or low productive oak coppice forests, have mostly available in Turkey. In the concept of modern forestry, the usage of oak coppice forest has great importance for sustainability. Additionally, due to being a developing country, the industry of Turkey has a huge capacity. While industrial production is high and getting increase, the number of industrial by-products have great capacity. Especially on the wood

processing industry, a large amount of industrial wood sawdust is generated that is one of the sources of lignocellulosic biomass.

The existing biorefineries that are first generation biorefineries in Turkey produce only one fuel, especially bioethanol or biodiesel, individual. However, third generation biorefinery is not built yet. Development of second and third generation biorefineries reduces fossil fuel consumption, decreases fossil dependency and improves energy security, creates new industrial sector and markets, provides new job opportunity for natives and contributes to sustainability and circular economy.

In the term of sustainability is “development that provides the demands of the present without compromising the capability of future generations to meet their own demands” and must be in balance with environmental, social and economic dimensions of human activity. The circular economy is one of the tools for sustainable development and aimed to preserve products, components, and materials at their greatest utility and value at all times approach to cradle-to-grave. In the circular economy concept, biorefineries have great potential and attention for using renewable raw materials, producing multiple products at the same line and containing waste management.

The barriers on biorefineries have to be overcome to contribute to sustainable development and the circular economy. Increasing biorefinery efficiency and producing multiple productions on the same line are vital factors to overcome the barriers. Through this purpose integrated biorefineries come to the forefront. Integrated biorefineries cover biorefineries which include process integration such as feedstock and product integration, heat and power integration, water integration, infrastructure process synthesis, and life cycle assessment (LCA), sensitivity analysis, supply chain, and strategic planning, policy and environmental integration. The integrated biorefineries that used organosolv pretreatment are named as integrated organosol based biorefinery (IOBB).

Process simulation is a fundamental tool due to cover both process synthesis and sensitivity analysis. It provides to design complicated processes close to actual conditions. In addition to process simulation, LCA is another main tool for process integration. LCA studies determine the environmental impacts of the process. In the combination of process simulation and LCA, it provides to obtain detailed material, and energy flow rates. These data could be used in the LCA study. LCA study reveals the environmental impacts of every step of production and high impacted categories can be determined and these categories are redesigned to reduce environmental impacts.

The aim of this thesis research is designing and simulating IOBB and determine the environmental impacts of simulated IOBB. For this purpose, two different feedstocks such as sessile oak coppice (SOC) and industrial wood sawdust (IWS) from Bursa/Turkey region are used to produce different products such as bioethanol, organosolv lignin, furfural, acetic acid, bioheat, and biopower. Accordingly, local feedstocks (SOC and IWS) are selected for reducing the cost of feedstock and reducing pollutant that occurred by transportation, cogeneration and wastewater treatment processes are integrated to IOBB for reducing the waste quantity and producing bioheat and biopower from waste. Then, to conduct LCA studies to determine the environmental sustainability of simulated case studies of IOBB. LCA results allow determining the contribution of process and products on environmental impacts. Additionally, LCA comparison with the most accessible and related organosolv based biorefinery that found in the literature is presented. To contain both process simulation and LCA of IOBB, this thesis research is the first study to our knowledge. Additionally, there is any existed biorefinery, and this study will be the first in Turkey. In the end, it will be a guiding light to all concerned about biorefineries.

The study begins with detailed literature research about biorefineries. According to literature studies, organosolv pretreatment method was selected as a pretreatment method. Therefore, for designing and simulating IOBB, Aspen Plus V8.8 simulation software was used. In order to present IOBB approach, organosolv pretreatment, furfural production, acetic acid recovery, enzyme production, saccharification and fermentation, distillation, wastewater treatment, and cogeneration processes were designed and simulated to produce bioethanol, organosolv lignin, furfural, acetic acid, bioheat, and biopower. In Aspen Plus simulation software, two different case studies were simulated. The SOC from Bursa region was used as feedstock of Case Study 1 (CS-1). In Case Study 2 (CS-2), the mixture of SOC and IWS was selected as feedstock. According to simulation results, 1160 kg/h of bioethanol, 908 kg/h of organosolv lignin, 340 kg/h of furfural, 122 kg/h of acetic acid, 7495 kW of bioheat and 2139 kW of biopower were produced in CS-1, while the results were 1155 kg/h, 894 kg/h, 358 kg/h, 135 kg/h, 7223 kW, 2064 kW in CS-2, respectively. Aspen Plus simulation software presents all material and energy balances for all streams. The results which were obtained from Aspen Plus, the Ecoinvent database, and literature, are used in SimaPo V8.1.1.16 LCA software to determine the environmental impacts of biorefineries. Goal and scope definition, system boundaries, Life Cycle Inventory (LCI) have been defined. Energy based allocation method and attributional LCA are selected in the LCA study. System boundary covers from feedstock transportation to end of production for 1 ton of dry feedstock. Based on the literature studies, ReCiPe midpoint method and endpoint methods were selected to determine environmental impacts. According to LCA results, the highest impacts for CS-1 and CS-3 which is found in the literature is occurred from organosolv pretreatment and for CS-2 are occurred from the cogeneration process. To compare case studies, while CS-2 has the highest impact on human health, CS-3 has the highest impact on the ecosystem and resources categories.

Aspen Plus simulation software and LCA results allow an overview to IOBB and provide to make technological improvements. These improvements enable the reduction of environmental impacts. Therefore, the eco-design approach is adopted. According to results organosolv pretreatment and cogeneration processes have major impacts on the environment and the modifications to reduce water and electricity consumption, and more efficient dryer selection on organosolv pretreatment process and reduce the water content in combusted feedstock, greener oven selection, and effective heat transfer between the reactor and air on the cogeneration process will reduce environmental impacts. This modification introduces the eco-design approach of IOBB and provides IOBB green technology and low carbon economy.

ENTEGRE ORGANOSOLV BAZLI BİYORAFİNERİ TASARIMI VE YAŞAM DÖNGÜSÜ DEĞERLENDİRMESİ: BURSA/ TÜRKİYE BÖLGESİNDEN SAPSIZ MEŞE (*Quercus petraea*) VE ENDÜSTRİYEL ODUN TALAŞI KULLANARAK DURUM ÇALIŞMALARI SİMÜLASYONU

ÖZET

Biyorafineriler, temelde geleneksel fosil rafinerilerine benzemekte olup hammadde olarak fosil yakıtlar yerine biyokütle kullanırlar. Biyorafineriler, biyokütleyi kimyasal ve biyolojik prosesler sayesinde biyoyakıt, biyogüç, biyokimyasal ve biyomalzemelere dönüştürürler. Literatürde biyorafinelerle ilgili birkaç sınıflandırma kabul edilmektedir. İlk olarak tanımlanan sınıflandırma hammadde/proses/ürün özelliklerine göre yapılmaktadır. Birinci nesil biyorafineriler tek hammadde kullanarak bir proseste bir ürün üretirler. İkinci nesil biyorafineriler, tek hammaddeden çeşitli prosesler sayesinde çeşitli ürün üretirler. Üçüncü nesil biyorafinerilerde çeşitli hammaddeler kullanılarak çeşitli proseslerden birden çok ürün üretilir. Bir diğer sınıflandırma, biyorafinerilerin kullandığı hammadde baz alınarak yapılmaktadır. Bu sınıflandırmada biyorafineriler, lignosellülozik hammadde biyorafinerileri, bütün-ekin biyorafinerileri, yeşil biyorafineriler, deniz biyorafinerileri ve iki platform biyorafinerileri olarak sınıflandırılmaktadır. Lignoselülozik hammadde biyorafinerileri, lignoselülozik biyokütleyi hammadde olarak kullanarak biyoyakıt, biyogüç, biyokimyasal ve biyomalzeme üretirler. Lignoselülozik biyokütle, içerisinde büyük oranda selüloz ve yanı sıra hemiselüloz ve lignin içeren tüm odunsu ve odun dışı biyokütleyi kapsar.

Lignoselülozik biyokütlenin zor ayrışan yapısı nedeniyle, lignini hemiselüloz ve selüloz fraksiyonundan ayırmak için ön işlem yöntemleri uygulanmalıdır. Ayrıca, ön işlemler selülozik yapının kristalliğini azaltır, biyokütlenin yüzey alanını arttırır, hidroliz ve fermantasyon sırasında inhibitör oluşumunu önler, işlem maliyetini azaltır ve enerji tüketimini azaltır. Ön işlem yöntemlerinin genel sınıflandırması; fiziksel ön işlem, fizikokimyasal ön işlemler, biyolojik ön işlemler ve kimyasal ön işlemlerdir. Organosolv ön işlemi, lignoselülozik biyokütle için en umut verici delignifikasyon yöntemlerinden biridir. Organosolv ön işleminin diğer ön işlemlerden temel farkı, ligninin diğer ön işlem yöntemlerinde atık olarak üretilmesine rağmen, organosolv ön işleminde neredeyse saf bir biçimde elde edilmesidir ve böylelikle lignin, değeri yüksek bir kimyasal olarak üretilir ve diğer kimyasal üretimleri için hammadde olarak kullanılır. Organosolv ön işlemi, organik çözücüler, asidik ya da bazik katalizörler varlığında eş zamanlı gerçekleşen bir delignifikasyon yöntemidir.

Türkiye'de biyokütlenin teknik potansiyeli çok önemlidir. Her ne kadar modern teknolojide biyokütle kullanımı yakın zamana kadar gelişmemiş ve çoğunlukla geleneksel yakma için kullanılmasına rağmen, biyokütlenin önemi günden güne ilgi çekici hale gelmiştir. Modern ormancılık, biyokütlenin biyorafineri alanında etkin bir şekilde uygulanmasını sağlar. Türkiye'de büyük ölçüde hem verimsiz hem de düşük verimli meşe baltalık ormanları mevcuttur. Modern ormancılık kavramında meşe baltalık ormanlarının kullanımı, sürdürülebilirlik için büyük öneme sahiptir. Ek olarak,

gelişmekte olan ülke olması nedeniyle, Türkiye sanayisi büyük kapasiteye sahiptir. Endüstriyel üretimin hem yüksek olması hem de artmaya devam etmesi, endüstriyel atık oranının da artmasına neden olmaktadır. Özellikle odun işleme endüstrisinde, büyük miktarda lignoselülozik biyokütle kaynaklarından biri olan endüstriyel odun talaşı üretilir.

Türkiye'deki biyorafineriler, genellikle tek bir ürün (biyoetanol ya da biyodizel) üreten birinci nesil biyorafinerilerdir. Üçüncü nesil yani aynı anda bir çok ürün üreten biyorafineriler henüz kurulmamıştır. İkinci ve üçüncü nesil biyorafinerilerin geliştirilmesi, fosil yakıt tüketimini azaltır, fosil bağımlılığını azaltır ve enerji güvenliğini arttırır, yeni sanayi sektörü ve pazarlar yaratır, yeni iş imkanı sağlar, sürdürülebilirliğe ve döngüsel ekonomiye katkıda bulunur.

Sürdürülebilirlik terimi, "gelecek nesillerin kendi gereksinimlerini karşılayabilme kapasitesinden ödün vermeden mevcut koşullarını sağlayan kalkınma" olarak tanımlanmaktadır ve insan faaliyetinin çevresel, sosyal ve ekonomik boyutları ile dengede olmalıdır. Döngüsel ekonomi, sürdürülebilir kalkınma için ürünleri, bileşenleri ve malzemeleri her zaman en büyük fayda ve değerlerinde muhafaza etmeyi amaçlayan ve beşikten mezara yaklaşımını kabul eden bir araçtır. Döngüsel ekonomi yaklaşımında, yenilenebilir hammadde kullanması, aynı anda birden çok ürün elde edilmesi ve atık yönetimi içermesi nedeniyle biyorafinerilerin potansiyeli büyüktür.

Sürdürülebilir kalkınmaya ve döngüsel ekonomiye katkıda bulunmak için, biyorafinerilerdeki engellerin aşılması gerekir. Biyorafineri verimliliğinin arttırılması ve aynı hatta birden fazla üretim yapılması, engellerin üstesinden gelmek için kilit faktörlerdir. Bu amaçla, entegre biyorafineriler ön plana çıkmaktadır. Entegre biyorafineriler, hammadde ve ürün entegrasyonu, ısı ve güç entegrasyonu, su entegrasyonu, altyapı, proses sentezi ve yaşam döngüsü değerlendirmesi (YDD), hassasiyet analizi, tedarik zinciri ve stratejik planlama, politika ve çevresel entegrasyon gibi proses entegrasyonlarını içeren biyorafinerilerdir. Organosolv ön işlem yöntemini kullanan entegre biyorafinerilere entegre organosolv bazlı biyorafineriler denilmektedir (EOBB).

Proses simülasyonu hem proses sentezi hem de hassasiyet analizini kapsaması nedeniyle entegre biyorafinerde kullanılan temel bir araçtır. Proses simülasyonu, gerçek koşullara yakın karmaşık proseslerin tasarlanmasına olanak sağlar. Proses simülasyonuna ek olarak YDD, proses entegrasyonu için başka bir ana araçtır. Prosesin çevresel etkileri YDD çalışmaları ile belirlenir. Proses simülasyonu ile ayrıntılı kütle ve enerji akış verileri elde edilir ve bu veriler YDD çalışmasında da kullanılabilir. YDD çalışması, üretimin her adımının çevresel etkilerini ortaya koymaktadır ve yüksek etkilenen kategoriler tespit edilebilmektedir ve bu kategorilerdeki çevresel etkileri azaltmak için yeniden tasarlama yapılabilmektedir.

Bu tez çalışmasının amacı EOBB'yi tasarlamak, simüle etmek ve simüle edilmiş EOBB'nin çevresel etkilerini belirlemektir. Bu amaçla, Bursa / Türkiye bölgesinden sapsız meşe korusu (SMK) ve endüstriyel odun talaşı (EOT) gibi iki farklı hammadde; biyoetanol, organosolv lignin, furfural, asetik asit, biyoısı ve biyogüç gibi farklı ürünler üretmek için kullanılmıştır. Buna göre, yerel hammaddeler (SMK ve EOT) hammadde ve nakliye maliyetini düşürmek için seçilmiş, kojenerasyon ve atık su arıtma prosesleri de atık miktarını azaltmak ve atıklardan biyoısı ve biyogüç üretmek için EOBB'ye entegre edilmiştir. Daha sonra, EOBB'nin simüle edilmiş durum çalışmalarının çevresel sürdürülebilirliğini belirlemek için YDD çalışmaları yapılmıştır. YDD çalışması sonuçları, EOBB proses ve ürünlerinin çevresel etkilerinin karşılaştırmasına olanak sağlamaktadır. Ek olarak, literatürde bulunan en uygun ve ilgili organosolv bazlı biyorafineri çalışması ile YDD karşılaştırması sunulmuştur. Bu tez çalışması, hem EOBB proses simülasyonunu hem de YDD çalışmasını içerdiği için, literatürde yapılan ve bilinen ilk çalışmadır. Ayrıca, biyorafineriler ile ilgilenen herkes için yol gösterici olacaktır.

Bu çalışma, biyorafineriler hakkında detaylı bir literatür araştırmasıyla başlamıştır. Literatür araştırmalarına göre ön işlem yöntemi olarak organosolv ön işlemi seçilmiştir. Bu nedenle, entegre organosolv bazlı biyorafineri tasarımı ve simülasyonu için Aspen Plus V8.8 simülasyon yazılımı kullanılmıştır. Entegre organosolv bazlı biyorafineri tasarımında, organosolv ön işlemi, furfural üretimi, asetik asit geri kazanımı, enzim üretimi, şekerleşme ve fermentasyon, distilasyon, atık su arıtma ve kojenerasyon prosesleri kullanılarak biyoetanol, organosolv lignin, furfural, asetik asit, biyoısı ve biyogüç üretimi tasarlanıp simüle edilmiştir. Bursa bölgesinden elde edilen SMK, Durum Çalışması 1 (CS-1)'in hammaddesi olarak kullanılmıştır. Durum Çalışması 2'de (CS-2), SMK ve EOT karışımı, hammadde olarak seçilmiştir. Simülasyon sonuçlarına göre, CS-1’de 1160 kg/saat biyoetanol, 908 kg/saat organosolv lignin, 340 kg/saat furfural, 122 kg/saat asetik asit, 7495 kW biyoısı ve 2139 kW biyogüç üretilmiştir. CS-2'de sonuçlar sırasıyla 1155 kg/s, 894 kg/s, 358 kg/s, 135 kg/s, 7223 kW, 2064 kW olarak bulunmuştur. Aspen Plus simülasyon yazılımı, tüm akışlar için tüm kütle ve enerji dengelerini sunmaktadır. Aspen Plus'tan elde edilen sonuçlar, Ecoinvent veritabanındaki veriler ve literatürde bulunan veriler ile birlikte biyorafinerilerin çevresel etkilerini belirlemek için SimaPo V8.1.1.16 YDD yazılımında kullanılmıştır. Amaç ve kapsam tanımı, sistem sınırları, yaşam döngüsü envanteri tanımlanmıştır. YDD çalışmasında, enerji bazlı çevresel etki paylaşımı yöntemi ve niteliksel YDD seçilmiştir. 1 ton kuru hammadde, temel birim olarak seçilmiştir. Sistem sınırı, 1 ton kuru ham madde için ham madde taşımacılığından üretiminin bitimine olarak seçilmiştir. Literatür çalışmalarına dayanarak, çevresel etkileri belirlemek için ReCiPe orta nokta yöntemi ve ReCiPe son nokta yöntemleri seçilmiştir. YDD sonuçlarına göre durum çalışmalarında proses karşılaştırılması yapılmış ve CS-1 ve CS-3 için insan sağlığı kategorisindeki en yüksek etkiler organosolv ön işleminden, CS-2 için kojenerasyon prosesinden kaynaklandığı tespit edilmiştir. Tüm EOBB simülasyonlarının karşılaştırması yapıldığında, CS-2 insan sağlığı üzerinde en yüksek etkiye sahipken, CS-3'ün ekosistem ve kaynaklar kategorisi üzerinde en büyük etkisi vardır.

Aspen Plus simulasyonu ve YDD çalışması EOBB’ye genel bir bakış yapılmasına ve teknolojik iyileştirmeler yapılmasına olanak sağlamıştır. Bu teknolojik iyileştirmeler, çevresel etkileri azaltmaya yöneliktir. Ekodizayn yaklaşımı benimsenmiştir. YDD sonuçlarına göre organosolv ön işlemi ve kojenerasyon prosesi çevre üzerinde en büyük etkilere sahiptir. Harcanılan su miktarının ve elektriğin azaltılması, daha verimli kurutucuların seçimi organosolv ön işleminde, yakılan madde nem içeriğinin düşürülmesi, verimli ve uygun fırın seçimi, reaktör ve hava arasında ısı transferini sağlayan ısı değiştiricinin verimli hale getirilmesi kojenerasyon prosesinde yapılacak değişikliklerdir. Bu değişiklikler, EOBB’yi düşük karbon ekonomisinde yeşil teknoloji kullanımına daha uygun hale getirir.

1. INTRODUCTION

Currently, the dependency on fossil fuel is overgrowing to provide energy demand due to industrial developments. 80% of the total energy demand of the world occurs from fossil fuel burning and fossil fuel dependency accompany with adverse effects on environmental, economic and social such as reducing oil reserves, unstable fuel price, climate change, decreasing air quality and increasing global temperature, political pressures and political security. All these reasons, force to nations, government and industries search an alternative fuel resource [1-5].

Renewable energy sources are one of the best alternatives to fossil sources. Renewable energy sources are that produces from a naturally renewing source [6]. Renewable energy sources provide economic development, protect the climate and provide energy security for countries [7]. The competition between fossil sources and renewable energy sources in three markets such as hot water and heating, power generation and transportation fuels are attractive [8]. Wind, solar, geothermal, hydropower and biomass are the renewable energy sources.

As one of the renewable energy sources, biomass is widely available, being environmentally friendly, long-term sustainable productivity, renewable, requiring lower cost than other fossil resources, suitable to produce biofuel, biopower, biochemical and biomaterial, beneficial to socio-economic development and ability to fix CO_2 from the atmosphere [9-13]. The term biomass describes entire carbonaceous materials which are produced biologically [14].

Biomass can be separated as primary and secondary products. Primary products generate photosynthesis that uses direct solar energy. Farm and forestry products, by-products of plants, residues and farm, forestry and industrial wastes are in the primary products. Decomposition/conversion of organic matters to higher organisms such as liquid manure and sewage sludge are the secondary products of biomass [15]. At modern bioenergy application, biomass sources contain forests, agriculture and waste/residues [13].

While fossil fuel covers 79.5 % of total energy demand, biomass energy covers 13% of total energy demand in the world [16]. Generally, the total primary energy supply in Turkey that is 145 Mtoe is met by oil (31%), natural gas (28%) and coal (28%) in 2017 [17]. While total native energy production was 35.357 million tons of oil equivalent (mTOE), total energy import was 124.425 mTOE, and total energy export was 7.853 mTOE [18]. 33.71 % of coal, 32.6% of gas and 24.56% of hydropower are used for electricity generation that is 273695 GWh in Turkey in 2016. To focus on the renewable energy source, the renewable electric generation that is 88610 GWh, hydropower is the leading energy source with 74.48%. Wind energy (17%) and geothermal energy (5.34%) follow it on renewable electricity generation [17]. According to statistics, fossil sources met 87% of total primary energy sources and 66.3% of total electricity generation. Due to prevent fossil dependency in Turkey, biomass has to bring to the fore. According to the International Renewable Energy Agency (IRENA), the total renewable energy and biomass energy capacity in 2017 were 2179 GW and 109 GW in the world, and 38 GW and 0.4 GW, in Turkey, respectively [19]. Although Turkey has great potential for biomass, the traditional usage of biomass covers biomass combustion to produce heat. Especially, forests are widely available in Turkey. Oak coppices are widely and readily available to use to produce biomass energy and biobased products in Turkey. It is reported that both unproductive or low productive oak coppice forests are the most promising feedstock for modern energy forestry in Turkey [20, 21]. Besides, Turkey is developing a country, and industrial developments are increasing. Wood processing is largely available in Turkey and by-products of wood processing industry can be a good alternative for biorefinery applications. In Turkey, modern energy application covers only combined heat and power (CHP) plants. There is any second or third generation biorefinery is existed in Turkey, currently.

There are several sustainable development definitions exist. However, the most accepted one is “development that provides the demands of the present without compromising the capability of future generations to meet their own demands” [22, 23]. Sustainable development has to be in balance with environmental, social and economic dimensions of human activity [24]. According to the United Nations General Assembly, sustainable development is formulated with 17 sustainable development goals which cover energy, economic growth, consumption and production, and climate action issues. Each interdependent goal has its targets, separately and their own goals [25].

The circular economy is dependent to sustainable development and exist in each step of the value chain such as production values from the cradle to the grave, maintenance and reproduction, waste control and management and reused secondary raw materials, by-products or waste as feedstock and contribute the economy [22]. In the business world, the circular economy is known that it is a restorative and regenerative frameworks which preserve products, components, and materials at their greatest utility and value at all times [26, 27]. Also, the circular economy transforms the end-life concept with decreasing feedstock, energy and time with alternatively reprocessing, recycling and recovering materials in each step of processes [28]. In the circular economy concept, biorefineries have great potential and attention for using renewable raw materials, producing multiple products at the same line and containing waste management.

Biorefineries are similar to traditional fossil-based refineries in terms of energy and chemical production. The fundamental difference of biorefineries is using from biomass to waste as a feedstock [29]. According to the International Energy Agency (IEA), the definition of the biorefinery is “the sustainable processing of biomass into a wide variety of biobased products such as food and feed, chemicals, materials and bioenergy such as biofuels, biopower, and bioheat” [30]. Biorefineries have to associate with economic and technical developments, environmental protection and social progress in providing sustainability and maximum resource efficiency [29]. Several classifications of biorefineries were determined. The first classification is based on the feedstock/process/product classification. This classification is known as generation classification. First generation biorefineries use single feedstock in a process and produce an individual product. Second generation biorefineries contain single feedstock, during multiple process and products. At last, third generation biorefineries used various feedstocks in different processes and produced several products [31]. The other classification is done according to feedstock such as lignocellulosic feedstock biorefinery, whole crop biorefinery, green biorefineries, marine biorefinery and the biorefinery two platforms concept [32].

LCFs are used lignocellulosic biomass as feedstock. The lignocellulosic biomass structure composes mainly sugar polymers such as cellulose and hemicellulose, and lignin [32, 33]. Lignocellulosic biomass has great potential to become the most significant biomass source due to being large availability, comparatively required less cost, does not compete with food and feed industry [34]. Lignocellulosic feedstocks are forestry products (softwood, hardwood, and forestry wastes), agricultural residues (straws, stovers, cobs, non-food seeds), industrial waste (food industry residues, timber industry residues, chips, and sawdust), domestic wastes (waste papers) and municipal solid wastes [35, 36]. The pretreatment methods are required to separate lignin and hemicellulose from cellulose fraction in lignocellulosic feedstock biorefineries [37, 38]. Additionally, pretreatment methods decrease crystalline structure of cellulose, improve the biomass surface area, prevent the inhibitor generation during hydrolysis and fermentation, reduce the cost of the process and decrease the consumption of conventional energy [3, 39-42]. The pretreatment method selection and chemistry affect the process efficiency, configuration, and cost. All pretreatment methods have benefits and drawbacks. Selection of the pretreatment methods considered benefits, drawbacks and the desired products combination [1].

The pretreatment method is classified as physical pretreatment (chipping, grinding, milling, and pyrolysis), physicochemical pretreatments (explosion with steam, ammonia fiber, and carbon dioxide, ammonia recycle percolation, liquid hot water, and microwave irradiation), biological pretreatments, chemical pretreatments (ozonolysis, acid pretreatment, alkaline pretreatment, oxidative delignification, wet oxidation, ionic liquids, and organosolv delignification).

The biorefinery which used the organosolv delignification method as a pretreatment method is called as organosolv based biorefinery. Organosolv pretreatment is a simultaneous pretreatment method to dissolve lignin in an aqueous organic solvent with the aid of a catalyst and separate lignin from cellulose and hemicellulose fraction. The main superiority of organosolv pretreatment than the other pretreatment methods is obtaining lignin in the nearly pure form [43-46].

The main products of organosolv based biorefineries are bioethanol, organosolv lignin, furfural, acetic acid bioheat, and biopower. Transportation fuel consumption is met 58% of bioethanol production. Therefore, bioethanol production has great importance for reducing fossil fuel dependency [2]. In current technology, first generation bioethanol is widely produced by sugar and starch feedstocks. Because of being competitive with the food and feed industry, the production of first-generation bioethanol is disputable. Second generation bioethanol is produced from lignocellulosic feedstock and does not compete with food and feed industry. Bioethanol is used in the internal combustion engine as fuel. Due to lignin is produced the nearly pure form in organosolv pretreatment, organosolv lignin obtained as valuable co-product. There are some applications of organosolv lignin in the industry exists such as vanillic acid, vanillin, syringic acid, and syringaldehyde [47]. One other product of organosolv based biorefinery is furfural and used in petroleum refineries and petrochemical industries, pharmaceuticals industries, food industries, manufactured rubber and resin industries [48, 49]. Furfural is formed in the pretreatment step in the presence of an acid catalyst for conversion of xylose [50]. Acetic acid is also produced simultaneously in organosolv based biorefinery for conversion of acetate. Acetic acid is an important chemical and solvent in the industry such as plastic, adhesives, textile finishes, latex paints, and vinyl acetate monomer [51]. The application of a cogeneration unit in organosolv based biorefinery, both bioheat and biopower are produced. Thus, the energy requirement of the biorefinery is provided by bioheat and biopower. The excess bioheat and biopower are sold to markets.

IOBB is similar to traditional organosolv based biorefineries. The main difference of integrated organosolv biorefineries includes at least one process integration such as feedstock and product integration, heat and power integration, water integration, infrastructure, process synthesis, and LCA, sensitivity analysis, supply chain, and strategic planning and policy and environmental integration [52, 53]. Process simulation is one of the most significant process integration due to involving both process synthesis and sensitivity analysis. Additionally, process simulation allows an investigation of complicated processes close to actual conditions [54].

Aspen Plus simulation software is commonly accepted and used simulation software in chemical engineering for designing and simulating processes. It is allowed to simulate from feedstock input to product output and provide material and energy balances. Although it includes its database, it provides manual input for chemicals, materials, and methods.

LCA is another tool for process integration and applied for estimating environmental effects of a product, process or comparing the environmental effects of different process and products. The application of LCA standardized by the International

Organization for Standardization (ISO) and defined as “environmental aspects and possible environmental impacts from the first to the end of a product life cycle from the raw material achievement during manufacture, consumption, end-of-life treatment, recycling, reuse and final disposal [55, 56]”. In guidelines, several methodologies are developed, and it provides to LCA practitioners to freedom. It causes interpretation widely and therefore to address various specific questions. Assumptions and selections have great importance in providing trustable results in LCA studies. In the literature, although LCA studies are generally focused on biofuels for transportation, the LCA studies of biorefineries with multiple products have to be developed.

The aim of this thesis research is designing and simulating IOBB and determine the environmental impacts of simulated IOBB. For this purpose, two different feedstocks such as sessile oak coppice (SOC) and industrial wood sawdust (IWS) from Bursa/Turkey region are used to produce six different products such as bioethanol, organosolv lignin, furfural, acetic acid, bioheat, and biopower. Design criteria are selected to maximize production efficiency and to minimize to waste production. Accordingly, local feedstocks (SOC and IWS) are selected for reducing the cost of feedstock and reducing pollutant that occurred by transportation. Cogeneration and wastewater treatment processes are integrated into IOBB for reducing waste quantity and producing bioheat and biopower from waste. Then, to conduct LCA studies to determine the environmental sustainability of simulated case studies of IOBB. The results of LCA present to a ranking of environmental impacts of IOBB processes and products. LCA results are allowed to determine the contribution of each process and products on environmental impacts. Additionally, LCA comparison with the most accessible and related organosolv based biorefinery that found in the literature is presented.

Containing both Aspen Plus simulation and LCA, this study is the first study in Turkey and one of the limited number of the study in the world. Additionally, there is any existed third generation biorefinery. It is designed as a pilot plant. However, it is obviously seen that this IOBB can apply in industrial-scale. It makes a huge contribution to on-site energy production, native and national resource usage, energy strategy and chemical industry. In addition, eco-design approach contributes the green technology and low carbon economy. In the end, it will be a guiding light to all concerned about biorefineries.

2. THEORETICAL STUDY

This chapter includes theoretical studies and literature reviews in the subtitles which are given below:

- Biomass sources
- Woody biomass
- Turkey’s energy outlook and biomass potential
- Biorefineries
- Biorefinery products
- Biorefinery classifications
- Lignocellulosic biorefineries and pretreatment methods
- Integrated organosolv based biorefinery overview
- Process simulation and Aspen Plus software
- Life Cycle Assessment and SimaPro software

Literature reviews are presented at the end of each subtitle. For literature review section, all national and international academic databases such as Science Direct, Web of Science, SpringerLink, Wiley, Scopus, Taylor & Francis, Ulakbim, The Scientific and Technological Research Council of Turkey (TÜBİTAK) Scientific Journals, the Council of Higher Education National Thesis Center (YÖK Ulusal Tez Merkezi), etc. were scanned and the articles which were fit to keyword such as “Lignocellulosic feedstock, pretreatment methods for wood, organosolv lignin, bioethanol, acetic acid recovery, furfural recovery, furfural production from xylose, organosolv based biorefinery, integrated biorefinery, aspen plus, designing biorefinery, lignocellulosic biorefinery, cogeneration, wastewater treatment of biorefinery, life cycle assessment, life cycle assessment reviews, life cycle assessment of biorefineries, etc.” were analyzed. Additionally, some studies which were not reached from academic databases were found in ResearchGate which a social networking application between scientists and researchers. The articles found in Researchgate are used with the allowance of the authors. In addition, a review article about organosolv based biorefineries published in the Journal of Renewable and Sustainable Energy during the thesis study [57].

2.1 Biomass Sources

Biomass sources are one of the most promising renewable sources and have great potential to use in bioenergy, biochemical and biomaterial production. Generally, biomass has low sulfur and ash content, and it is accepted that contributes net zero atmospheric greenhouse gas (GHG) on a full life-cycle basis [58]. While traditional biomass is commonly used traditional heating by combustion, modern biomass provides to an application in modern biotechnology [59]. The term biomass defines biologically produced materials. However, in bioenergy applications, biomass is generally obtained from three areas such as forests, agriculture and wastes/residues. In addition to these areas, algaculture is developing the area to originated biomass source in bioenergy applications [12]. While biomass is a general term that accepted by authorities, there is any standard classification agreed [58]. Therefore, several different classifications can be found in the literature. Therefore, biomass classification is presented in Table 2.1 based on this study.

Also, according to one other classification, biomass sources are divided into two main groups such as woody and nonwoody biomass. While woody biomass contains lignocellulose that originated from forests, agriculture, and water/residues, non-woody biomass contains lignocellulose, sugar, starch, and oil that originated from agriculture and wastes/residues [13].

2.2 Woody Biomass

Woody biomass covers the untreated wood such as traditional wood for combustion, forest residues, collapsed and dead trees, industrial residues (chips, sawdust, and barks), agricultural residues from fruit trees, wood wastes from industrial wood processing and municipalities. Woody biomass is also known as lignocellulosic biomass due to contains lignocellulose. Lignocellulose is used to describe cellulose, hemicellulose and lignin structure in biomass [62].

Cellulose is the principal component in lignocellulosic biomass and provides toughness and elasticity to the plant cell walls and the fibers. Cellulose is a linear polymeric chain that β-1,4-glycosidic linkages connect β-D-glucopyranose (glucose) units. Generally, the degree of polymerization ranges from 500 to 1500 in cellulose.

Table 2.1 : Biomass classification based on the origin, adapted from [12, 58, 60, 61].

Biomass Source	Origin	Examples
Untreated Wood	Forest operations	Conventional combustion wood Forest residues
	Non-forest operation	Untreated wood residue
	Natural residues in forests	Collapsed and dead trees
	Wood processing industry	Industrial residues such as chips, sawdust, and barks
Energy Crops	Energy forestry	Short rotation forestry (SRF) and coppice (SRC)
	Energy agriculture	Fiber plants Grasses Carbohydrate plants Oilseed plants Aquatic (marine) plants
Agricultural Residues	Harvesting and processing	Fruit tree branches, straw, root, nutshells, husk
Waste and Residues	Animal waste	Animal manure
	Municipal waste	Organic wastes, treated urban wood wastes, sewage sludge
	Industrial waste	Organic wastes and residues

Thus, cellulose is an amorphous and crystalline structure [63]. The structure of cellulose is presented in Figure 2.1.

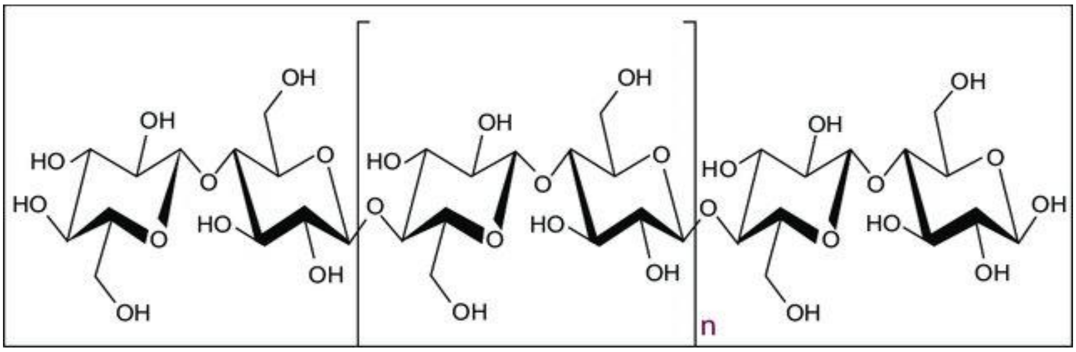


Figure 2.1 : The chemical structure of cellulose [64].

Hemicellulose is also a polymeric structure that found in lignocellulosic biomass. Like as cellulose, hemicellulose also provides the strength to the lignocellulosic biomass. Hemicellulose includes five main sugar monomers such as glucose (D-glucose), xylose (D-xylose), galactose (D-galactose), arabinose (L-arabinose), and mannose (D–mannose). In addition to main sugar monomers, rhamnose, glucuronic acid, methyl-glucuronic acid, and galacturonic acid are found in lignocellulosic biomass in a small amount. The degree of polymerization of hemicellulose is nearly 200 that is comparatively less than cellulose. While being more amorphous than cellulose, the conversion of hemicellulose to monomer sugars by the catalyst or enzymes more readily. However, some degraded products such as furfural and 5-HMF are formed during pretreatment [63]. Figure 2.2 shows the monomeric sugars in the hemicellulose structure.

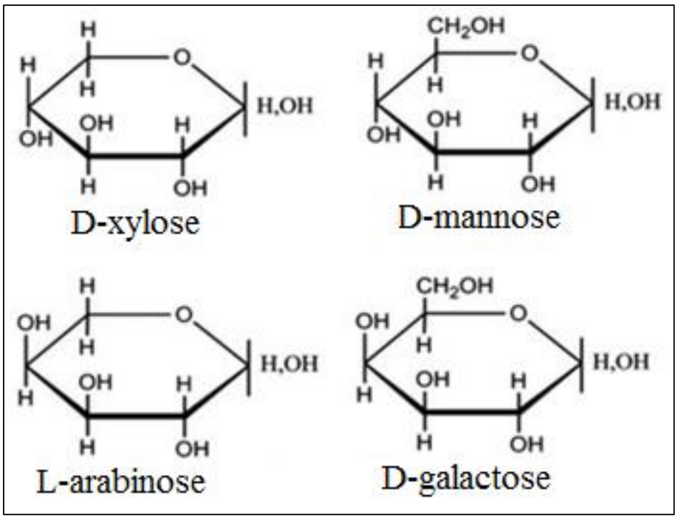


Figure 2.2 : Chemical structure of monomers of hemicellulose [65].

Lignin is the other abundant content in the lignocellulosic biomass, and it is phenolic compound and composed of phenylpropenyl (C9) units randomly. Three main alcohol monomers are coumaryl, coniferyl, and sinapyl alcohol linked to phenylpropenyl units [66]. The complex structure of lignin is varied depending on the biomass source. Except for conventional combustion of lignin, syngas derived chemicals and aromatics are the other application areas of lignin [67]. The chemical structure of lignin is illustrated in Figure 2.3.

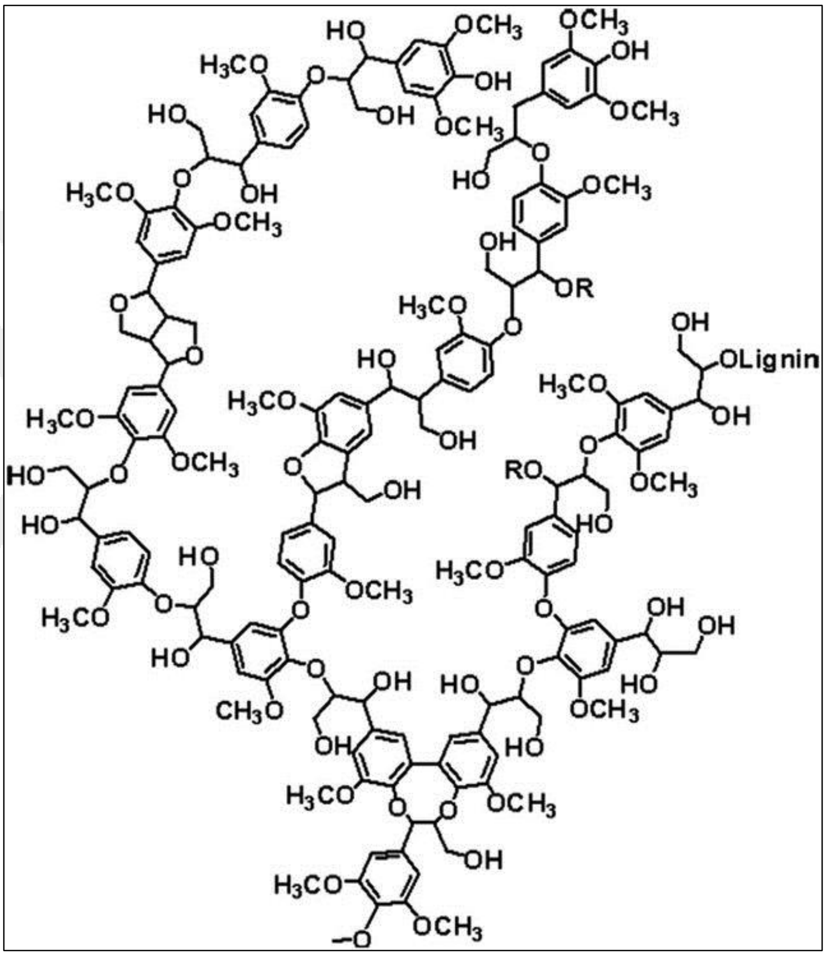


Figure 2.3 : The chemical structure of lignin [62, 63, 68].

The composition of lignocellulosic biomass generally contains 50-60% of carbohydrates which includes cellulose and hemicelluloses and 20-35% of lignin [69]. The compositions of some lignocellulosic biomass are given in Table 2.2.

Lignocellulosic biomass provides the most abundant potential volume and the lowest cost for biofuel and biochemical production [79]. While woody biomass originated by mostly lignocellulose, non-woody biomass also occurs a comparatively small amount of lignocellulose.

Table 2.2 : Composition of lignocellulosic biomass.

	Composition, w/w (%)			
Lignocellulosic Biomass	Celulose	Hemicellulose	Lignin	Reference
Barley Straw	42	28	na	[70]
Corn Cobs	45	35	15	[71]
Corn Stover	38	26	19	[72]
Cotton Seed Hairs	80-95	5-20	0	[71]
Grasses	25-40	35-50	10-30	[71]
Hardwood Stems	40-55	24-40	18-25	[71]
Indian Grass	39	29	na	[73]
Leaves	15-20	80-85	0	[71]
Miscanthus	43	24	19	[74]
Newspaper	40-55	25-40	18-30	[71]
Nut Shells	25-30	25-30	30-40	[71]
Oat	40	28	18	[75]
Paper	85-99	0	0-15	[71]
Pearl Millet	25	35	3	[76]
Poplar	49.9	25.1	18.1	[77]
Reed Canary Grass	24	36	2	[76]
Rice	40	23	15	[75]
Rye Straw	31	25	na	[73]
Softwood Stems	45-50	25-35	25-35	[71]
Sorghum	23	14	11	[75]
Soybean	33	14	na	[78]
Sugarcane Baggase	40	21	18	[75]
Switch grass	45	31.4	12	[71]
Wheat Straw	38	29	15	[70, 71]

2.2.1 Forest biomass

Forests have a significant environmental impact on protecting marginal land and decreasing CO_2 levels in the atmosphere. Softwoods and hardwoods are the main two types of forest biomass. Softwoods derived from conifers and gymnosperm trees. The density of softewoods is smaller and being mature of softwoods are faster than hardwoods. Pine, juniper, cedar, spruce, yew, cypress, fir, hemlock and redwood that are evergreen species are the example of softwoods. Poplar, maple, walnut, willow, oak, cottonwood, and aspen are some species of hardwoods and found in the Northern hemisphere, generally [62].

The woody biomass which occurs from forests is named as forest biomass. Forest biomass is the most widely terrestrial biomass and among the most biologically valuable and genetically diverse ecosystems in the world [80, 81]. Woody biomass has flexibility in harvesting time that does not affect by seasonal differences, unlike agricultural plants. Besides, the lower ash content, higher density, economical transportation due to strong structure make forests more advantageous than agricultural crops [62].

The classification of forest biomass includes two categories such as untreated and treated wood. Municipalities and wood processing industry wastes are treated wood. Conventional wood for combustion (firewood), wood from energy forestry and residues such as logging, natural disturbances, wood processing industries that contain no chemical are untreated woods [82]. Forests are used in both industrial and energy usage. This study focuses on the energy usage of forests.

2.2.1.1 Forests in Turkey

The forests in Turkey are mostly (99.9%) state-owned, and forestry issues are dependent on the government. General Directorate of Forestry (GDF) which is associated with The Ministry of Forestry and Water Affairs (MoFWA), is responsible for forest managing, security, production, recruitment, rehabilitation, and utilization.

According to the statistics published by the Republic of Turkey GDF, in 2018, 28.6% of Turkey’s surface area (22.342.935 ha) is covered with forests [83, 84]. 54% of this area (11.919.061 ha) is productive high forest, 3% (785.087 ha) is productive coppice forest, 34% (7.700.657 ha) is degraded high forest and 9% (1.938.130 ha) is degraded coppice forests [85]. Turkey has different forest types. The main species are given in Figure 2.4. The distribution of forests by species is shown in the chart below.

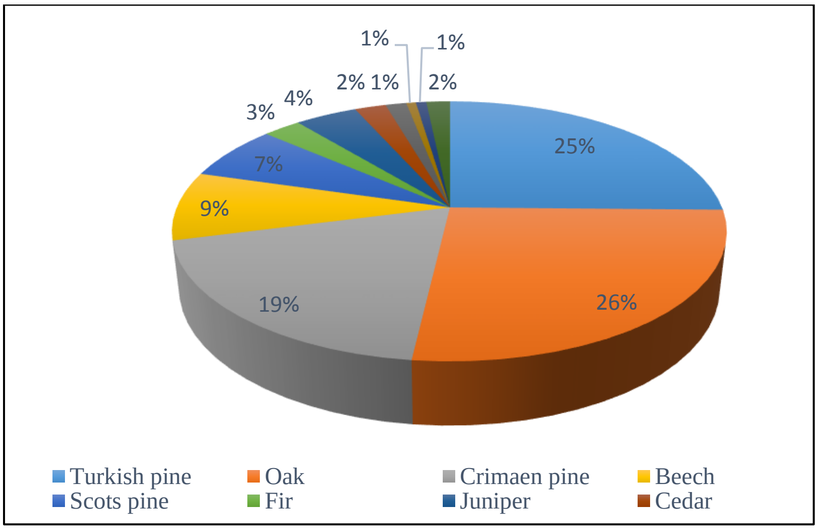


Figure 2.4 : Distribution of forest by species in Turkey [85].

As it is seen in Figure 2.4 the most widespread species in Turkey is oak (26%). Then, Turkish red pine (25%), Crimaen pine (19%), beech (9%), Scots pine (7%) and juniper (4%) follow the oak forests, respectively [83, 85]. In Turkey, the functions of the forest are 50% of economical usage, 42% of ecological usage and 8% of socio-cultural usage. According to statistics, the amount of carbon capture by forests was calculated as 1.910.762.195 ton/year, and oxygen production was 42.035.726 ton/year [83].

2.2.1.2 Energy forestry in Turkey

The modern energy forestry application had started in Canada and Sweden in 1970s. Recently, modern energy forestry is found a rapidly increasing attention around the world. Being environmentally friendly, renewable, local, and reducing GHG make energy forestry sustainable and clean energy resources [86].

The term of energy forestry is forest plantations solely for energy production [87]. With this purpose, fast growing and high calorific valued tree species are selected. Unlike conventional forests, 3 to 5 years are required as harvesting time. Generally, wood production from energy forestry is 20-60 t/ha.y [86].

In Turkey, energy forestry has been developed for 30 years and only to meet the firewood demand. The current aim of energy forestry in Turkey is decreasing and removing firewood demand from high forests [86].

In energy forestry, the species that grow 2 to 5 years are classified as short rotation coppice (SRC) and the species that grow 8 to 20 years are classified as short rotation forestry (SRF). The term of coppice defined the species that new sprouts regrow after the plant is cut down. Therefore, SRC is the coppices which are fast growing. SRC cultivation requires low-input agricultural requirements and due to low chemical application, implies low GHG emissions. The pesticides application is inappreciable and generally is not applied. Additionally, fertilizer usage is lower compared to conventional agricultural crops. Besides, SRC helps to increase water quality, enhances biodiversity, provides ecosystem services, prevents animal diseases between farms, prevents erosion, decreases synthetic input materials and reduces climate change due to carbon capture [88].

According to reports published by GDF, 562513 ha of energy forest had been established the years between 1978 to 2006. Although 27% of the total forest area is occurred from SRC, this ratio increases as 89% for oak forests. The oak coppices are the widest available species in Turkey [89].

2.2.1.3 Oak coppice forests in Turkey

Oaktree or shrub is in the *Quercus* genus and belongs to the beech family, *Fagaceae*. Oaks can exist as 20, 30 or 55 meters of high tree or shrubs according to their species. It can be monoecious, evergreen or deciduous form. The proportion occurs from seeds or vegetative. Barks are smooth, deeply furrowed or scaly. Some species are evergreen and some of are deciduous. The fruit is acorn annually or biennially. In the world, 600 species of oak are found, and nearly 400 species are in the northern hemisphere [90]. Oak forests are found in almost every region in Turkey. The diversity of species presents different alternatives of oak forests. Generally, oaks are divided into three groups due to the structure of anatomy, periods of fruit ripening, types of leaves and properties of barks [91].

- White oak
    - Sessile oak – *Quercus petraea*
    - European oak or English oak – *Quercus robur*
    - Strandzha oak – *Quercus hartwissiana*
- Red oak
    - Lebanon oak – *Quercus libani*
    - Macedonian oak – *Quercus trojana*
    - Turkey oak – *Quercus cerris*
- Evergreen oak
    - Kermes oak – *Quercus coccifera*
    - Holm oak – *Quercus ilex*
    - Boz-Pirnal Oak – *Quercus aucheri*

Turkey is a rich country for oak species and grows 18 species. With four subspecies and one variety species, the entire 23 different genera of oak are found in Turkey [92]. The total area of oak forest in Turkey is 5886195 ha and are found in all regions of Turkey. Table 2.3 shows the distribution of oak forest by regions in Turkey. The oak forest area is 26% of the total forest area of Turkey. As it is seen from Table 2.3 that, oak forests are widespread through the country. Productive high forest for oak forests in Turkey is 17%, degraded high forests are 17%, productive coppice forests are 23.8%, and degraded coppice forests are 41.6% [91].

Table 2.3 : Distribution of oak forest by regions in Turkey [93].

Region	Oak Forest Area (ha)
The Marmara Region	939632
The Aegean Region	479066
The Black Sea Region	1041651
The Mediterranean Region	234855
The Central Anatolia Region	669236
The Eastern Anatolia Region	1304960
The Southeastern Anatolia Region	1216795
Total	5886195

2.2.2 Industrial waste and residues

Lignocellulosic biomass which obtained from industrial waste and residues is generally originated from industrial wood processing. The term of industrial wood processing described as the conduct processing technologies that contain cut, grinded, compressed, milled, machined of timber. Sawdust is the typical product of industrial wood processing due to small particles originate during industrial wood processing [94].

2.2.2.1 Industrial wood sawdust

Wood processing industries, use wood as feedstock and convert it into valuable products. Wood processing industries such as milling and crushing of wood, plyboard, wood panel, household equipment, construction and its components, surface coating, particle board, wall pointing, and craft industries produced an enormous number of by-products such as woody sawdust and wood chips [95]. Traditionally, these by-products are used in combustion for producing heat. However, chemical conversion technologies provide to convert wood sawdust into value-added products.

According to technological developments and customer preferences, furniture is not produced by pure timber or wood. Generally, two kinds of woody material are used such as Medium Density Fiberboard (MDF) or chipboard. The finest particles called sawdust and sawdust is compressed with high pressure, and MDF is produced. MDF has a higher quality than chipboard. Chipboard is also compressed with high pressure; however, their particles are larger (chips), and quality is lower than MDF. Some adhesives are added during MDF and chipboard production. Both MDF and chipboard are covered according to customer preferences before furniture manufacturing. Because of including adhesives and dyes, MDF and chipboard are not convenient for biofuel production. Sawdust and chips are appropriate for use as a woody biomass source for biorefineries.

This thesis study focuses on untreated woody biomass that originated from the forest (sessile oak coppice) and industrial wood processing (industrial wood sawdust).

2.3 Turkey’s Energy Outlook

The Republic of Turkey is a developing country located in both Europe and Asia and has strategic location due to being as a bridge between these continents. In the ranking of the largest economy, Turkey is the 17th position in the world and 6th in Europe. Therefore, energy consumption is highly growing [96]. According to Key World Energy Statistics 2017 Report, Turkey is on the fifth rank on most natural gas importer countries in the world and seventh rank on most coal importer countries in the world [97]. The energy supply is increasing due to economic and industrial developments. The total primary energy supply was 32 Mtoe in 1977, 72 Mtoe in 1997 and 145 Mtoe in 2017. The total primary energy supply by the source in Turkey is illustrated in Figure 2.5.

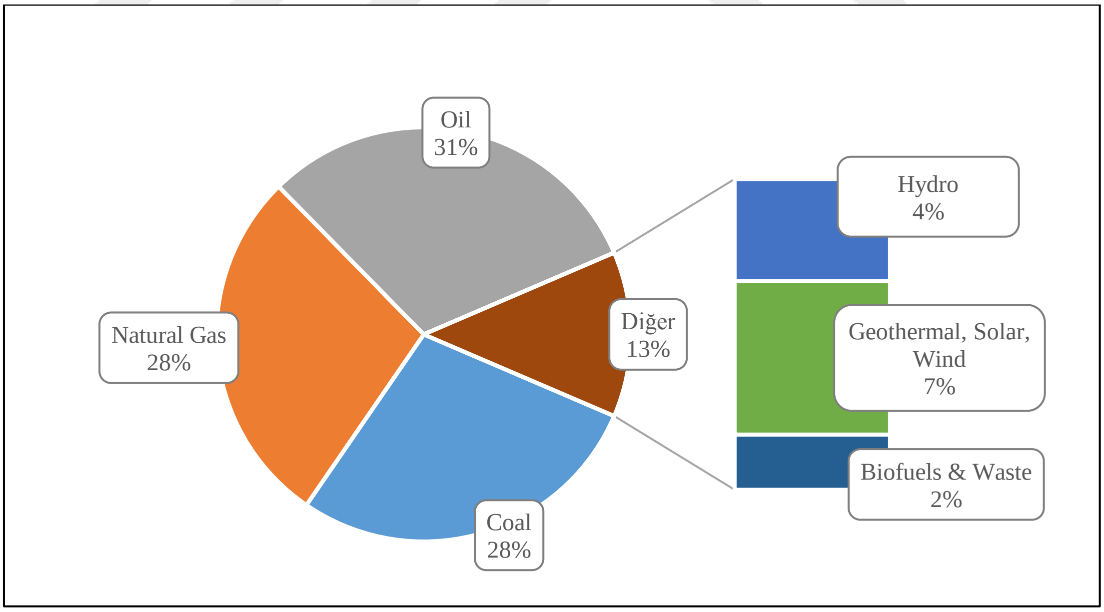


Figure 2.5 : Total primary energy supply by the source in Turkey in 2016 [17].

According to Figure 2.5, the highest share on total primary energy supply is on oil with 31% (42.110 Mtoe). Coal and natural gas follow oil with 28%. Coal and natural gases are 38345 ktoe and 38262 ktoe, respectively. Renewable energy sources have 13% of share and contain hydropower (5.781 Mtoe), geothermal, solar and wind (8681 toe) and biofuels and waste (3.120 Mtoe). According to 2016 statistics, electricity generation by fuel in Turkey is presented in Figure 2.6.

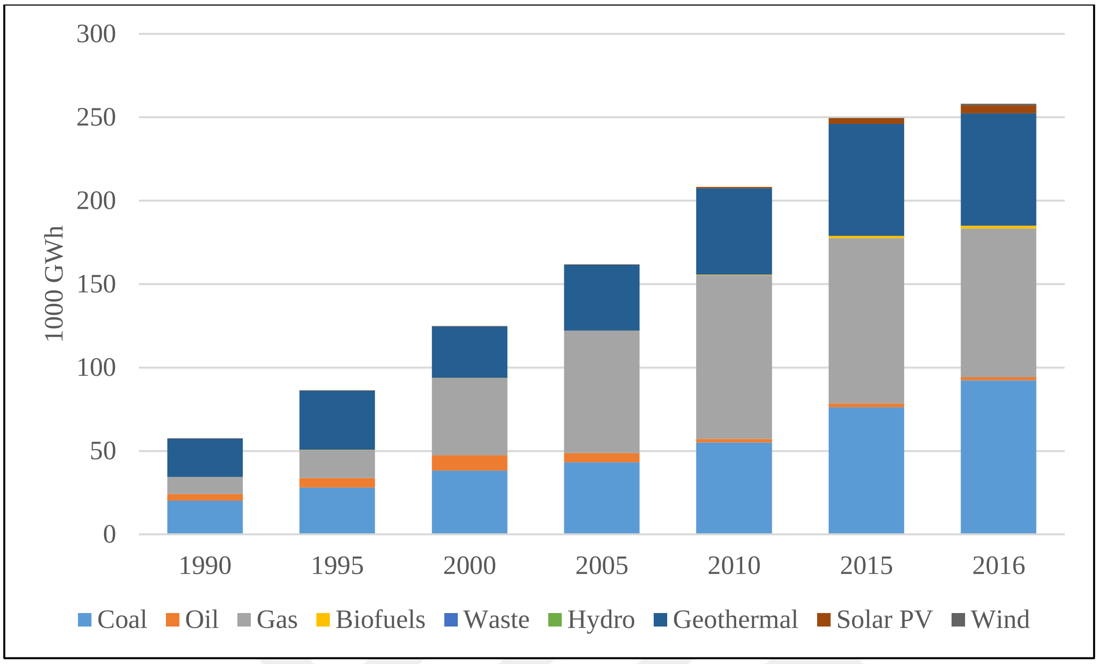


Figure 2.6 : Electricity generation by fuel in Turkey in 2016 [17].

Total electricity generation in Turkey is 273695 GWh in 2016. Electricity demand is mostly met by coal (92273 GWh) and natural gas (89227 GWh). Next, hydropower follows them with 67231 GWh. Other renewables such as wind (15517 GWh), geothermal (4819 GWh), solar photovoltaic (PV) (1043 GWh), biofuels (1635 GWh) and waste (24 GWh) are entirely meet to 8.42% of total electricity generation. While hydropower is included, total renewable energy sources for electricity generation is 32.94%. 87% of the total primary energy supply and 66.31% of total electricity generation are met by fossil source. It is seen that the fossil dependency of Turkey is very high. Consequently, the importance of renewable energy sources should be increased to reduce fossil dependency on Turkey. Figure 2.7 presents renewable based installed power capacity annually.

Figure 2.7 indicates that, while the installed power capacity was 13606.8 MW in 2007, it increased by nearly 300% and improved as 38907.2 MW in 2017. These results showed that the attraction of renewable energy sources is increasing. Renewable based installed capacity contains hydropower with 27273.1 MW, wind with 6516.2 MW, biomass sources with 634.2 MW, geothermal with 1063.7 MW and solar PV with 3420 MW. While hydropower is the driven force for electricity generation, electricity generation from wind has great advance in recent years.

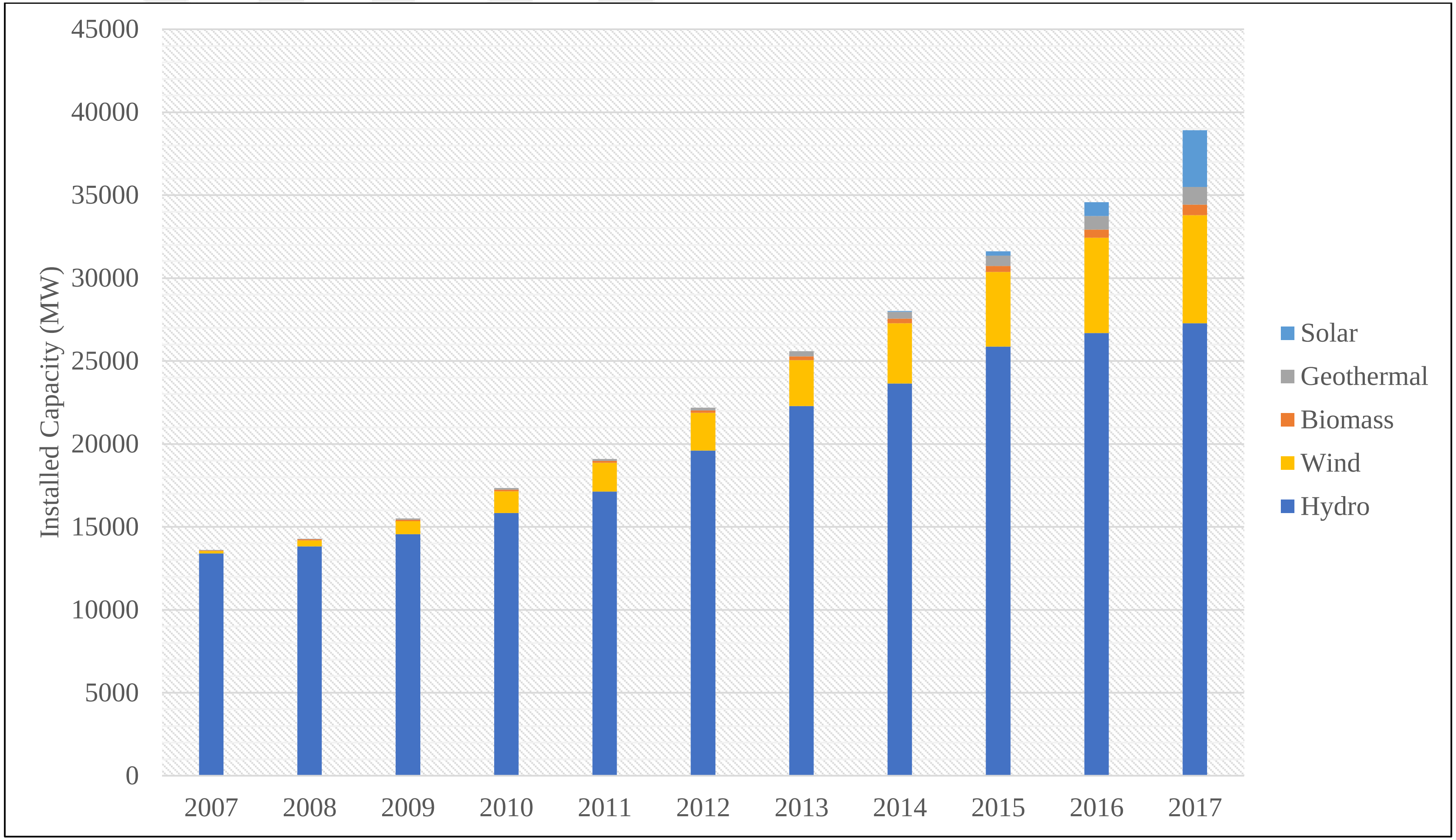


Figure 2.7 : Annually renewable based installed power capacity [98].

Additionally, solar PV has an attractive increase since 2016. Biomass source has the lowest installed power capacity in Turkey. renewable energy sources based gross electricity generation in Turkey in 2016 is illustrated in Figure 2.8.

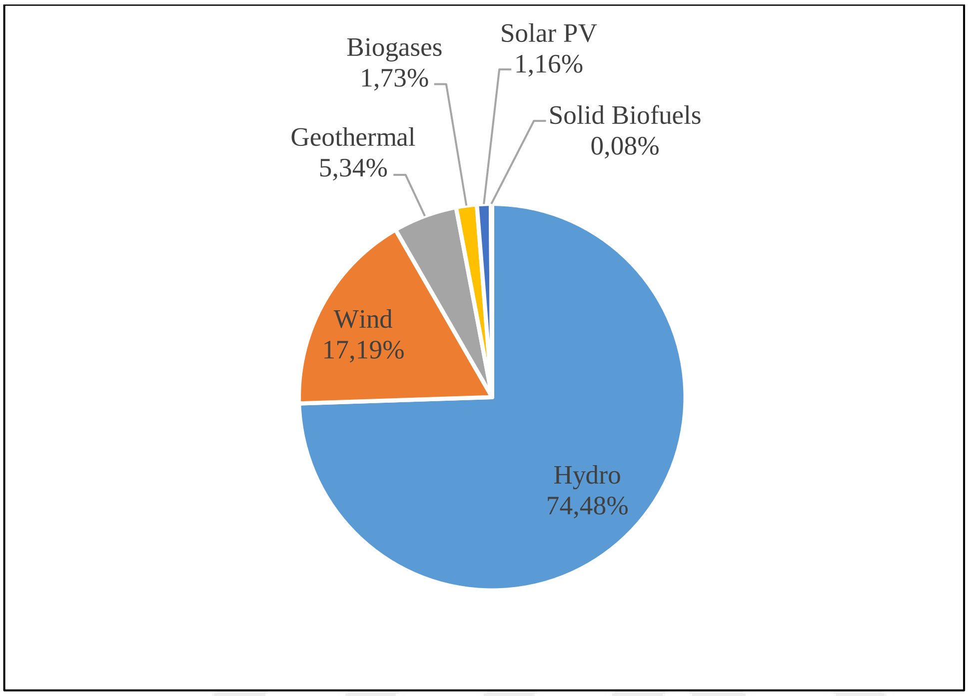


Figure 2.8 : Gross electricity generation from renewable energy sources in Turkey in 2016 [17].

Renewable energy sources based electricity generation is 88610 GWh in 2016. Three out of four of electricity generation is met by hydropower (67231 GWh). It was followed by wind energy (15517 GWh), geothermal energy (4819 GWh) and solar PV (1043 GWh) in 2016. Thermal solar energy and tide energy are not used for electricity generation in Turkey. 3.216 GWh electricity had generated from biomass based electricity production plants that have 811 MW installed capacity in 2018. The potential of forestry waste and residues is 1.5 Mtoe, and agricultural biomass potential is 303.2 PJ in Turkey [98].

To reduce fossil dependency, the Government of Turkey had developed the National Action Plan by 2023. The national target of a share of renewable energy sources will improve 30% of total installed power in 2023 [96].

Besides electricity generation, transportation is another fundamental category for energy consumption. Figure 2.9 presents the fuel usage ratios in the transportation sector in 2016.

Table 2.4 : Targeted renewable based power generation installed capacity in Turkey [98-100].

Renewable-based Power Generation	Installed Capacity (MW_e)	National Targets (MW_e)	
	2018	By 2019	By 2023
Hydro	27273.1	32000	34000
Wind	6516.2	10000	20000
Biomass	634.2	700	1000
Geothermal	1063.7	700	1000
Solar	3420	3000	5000
Total	38907.2	46400	61000

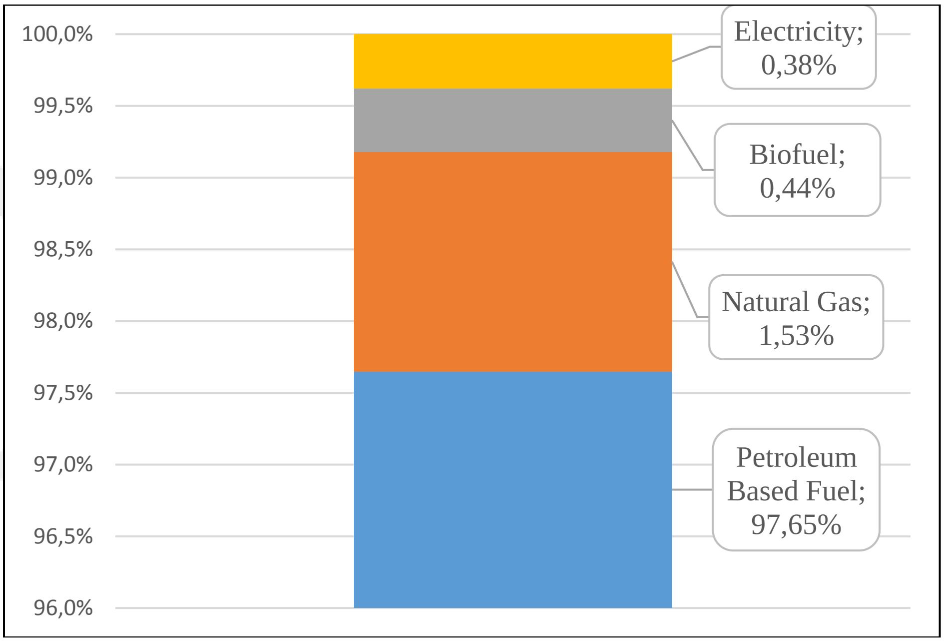


Figure 2.9 : Energy supply for transportation sector in Turkey in 2017 [18].

In Turkey, the transportation sector mainly depends on fossil based fuels such as gasoline and diesel. 2.5 Mtoe fuel was consumed in 2017 in Turkey. 27.8 Mtoe of transportation fuel is based on petroleum. 0.4 Mtoe of fuel is met by gas. Biofuel and electricity usage in the transportation sector is 0.82%, and it is equal to 0.2 Mtoe. Fossil fuel dependency is also high in the transportation sector.

In Turkey, third generation biorefineries are unconstructed. Only, one type of biofuel produced biorefineries exists. According to the Republic of Turkey, the Ministry of Agriculture and Forestry, the Department of Tobacco and Alcohol, only three companies have fuel aimed for bioethanol production and distribution license in Turkey. These companies are TARKIM Agricultural Chemistry Inc. (Bursa), TEZKIM Agricultural Chemistry Inc. (Adana) and Konya Sugar Plant Inc (Konya)

[101]. The total bioethanol production in Turkey is 162 million liters, and 76 million liters of bioethanol is used for fuel. 92% of total bioethanol is used in Turkey as a fuel additive, and 8% of bioethanol is exported [101, 102].

2.4 Biorefineries

Biorefinery concepts are focused on the usage of the entire plant or complex biomass and consolidation of a traditional and new process for using biological feedstocks, currently. However, at the end of the 19th and the beginning of the 20th-century, industrial biorefineries were based on pulp and paper production, saccharification, guncotton and viscose silk production, and the furfural production. Also, the sugar and starch production, oil milling, the separation of proteins for feed production technology, etc. had great importance in history. In 1748, A.S. Marggraf had published a study on the separation of crystalline sugar from various biomass, and F.C. Achard was developed first sugar beet refinery in 1801, in Poland. In 1811, G.S.C. Kirchhoff invested that starch in potato converted to grape sugar when cooked in dilute acid. In 1812, the first starch biorefinery was implanted in Germany. In 1819, H. Braconnot invented that glucose is generated by concentrated sulfuric acid in treated wood. In 1835, J.J. Berzelius invested enzymatic hydrolysis of starch to sugar and named it as “catalysis”. G.F. Melsens stated that this conversion could also be formed in dilute acid in 1855. A. Mitscherlich developed the sulfite pulp process to produce ethyl alcohol by fermentation of sugar in 1878. A first commercialized process named as wood saccharification by sulfuric acid established in 1901 and by dilute sulfuric acid in 1909. T. Kingsford established a corn based biorefinery in New York the 18th century. The extensive usage of green crops had started with Osborn in 1920, and Slade & Birkinshaw extracted green crops to produce proteins in 1939. N.W. Pirie investigated the mechanical division and extraction methods required to utilize of green crops. A fundamental historical step for current biorefinery developments was “Chemurgy” which included industrial and political approaches founded in 1925. Chemurgy is shortened of “chemistry” and “ergon” which means work in the Greek language. The meaning of chemurgy is chemistry from an acre, and it is a connection between agriculture and chemical industry. Chemurgy was shown to have a vital industrial and political aspects that aimed at the usage of agricultural resources; now it is known as renewable resources in the industry. Also, in 1935 a national council which is called “National Farm Chemurgic Council” had a conference between agriculture, industry, and science. After World War II, a high number of crude oil based inventions and productions processes remained, and the end of Chemurgy started. Henry Ford introduced a car in 1941. The internal coating and external body were produced 100% of biosynthetics. This car was combusted with methanol which produced by pyrolysis from cannabis. Primarily, researchers from Ford Company had investigated more than 30 soybean based industrial products. Between the year of 1935 and 1960, some biorefineries were implanted in Germany and the US [32].

Although some of being superior technologies, most of the technologies which are mentioned above on the competition with fossil resource technology and economy, renewable based technology fall behind. However, when the oil crisis happened, higher fossil fuel prices and having a deep impact on the environment, technical and economic cooperation between agriculture, forestry, and food production industry has started again in the 1970s.

The term of biorefinery was defined in the 1990s [32]. In today’s situation, the attention of renewable carbon from biomass is increased, and renewable carbon from biomass takes fossil-based carbon’s place. These reasons lead to the development of biorefineries which biofuels, bioenergy, biochemicals, biomaterials, food, and feed are efficiently co-produced [103]. Biorefineries provide flexibility of feedstock requirements and advanced energy efficient production compared to single fuel production [79]. Figure 2.10 gives details about basic principles of biorefineries.

As it is seen clearly in Figure 2.10, the primary feedstock of biorefineries is biomass. First of all, physical pretreatment has to applied biomass before conversion. Physical pretreatment contains grinding, milling, chipping and pressing. In physical pretreatment, biomass dimensions are minimized, and particle surface area is increased. Solid biofuels such as biobriquette, biopellet, woodchips, and firewoods are produced directly by physical pretreatment. With biochemical (fermentation, anaerobic or aerobic digestion, enzymatic hydrolysis) and thermochemical conversion (combustion, co-firing, gasification, pyrolysis, carbonization, liquefaction), value-added products such as biochemicals, biofuels, biopower, and biomaterials can be produced from biorefineries. Also, end-products of biofuels can be varied as solid, liquid and gaseous fuels for biofuels [12].

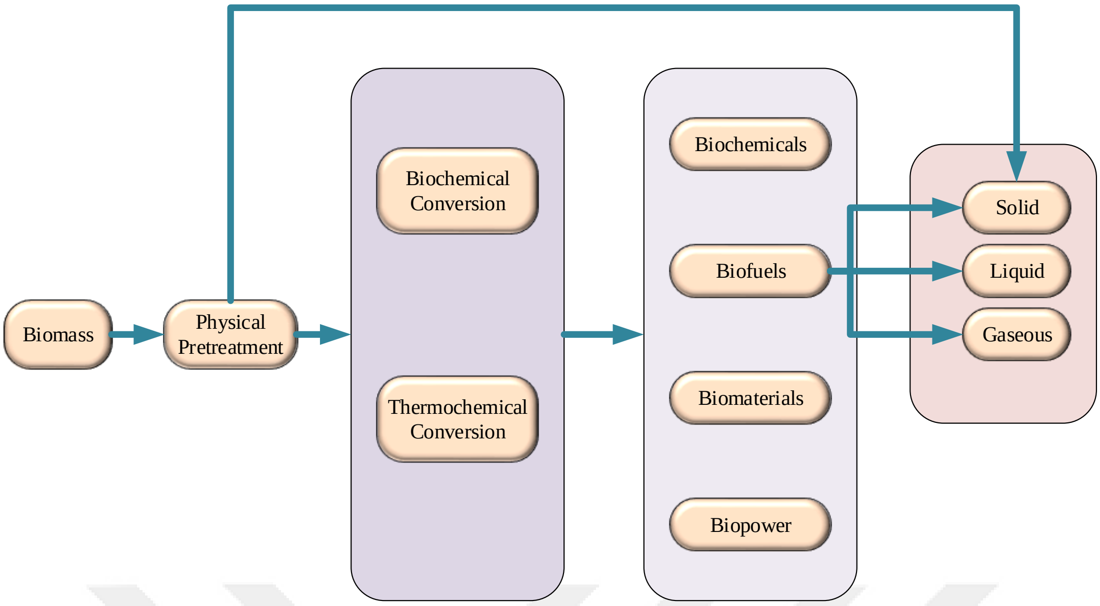


Figure 2.10 : Basic principles of biorefinery technologies, adapted from [12].

2.5 Biorefinery Products

The term of biorefinery product describes to products which are derived from biomass in the biorefineries by the aid of chemical and biological conversions. Recent biorefinery technologies provide an opportunity to produce commercial biobased products such as biofuels, biochemicals, biomaterials, and biopower. These products have critical importance in the circular economy where the value of all inputs and outputs are promoted in the economy, and the waste formation minimized, is a significant contribution to the European Union (EU)'s efforts on sustainability, carbon reduction, the efficiency of resource and competitive economy. Each step from production to recycling or production of residual waste are resubmitted into the economy [104]. Biorefinery products are used to replace fossil based products. Industrial applications, transportation, textiles, food supply safety, environmental application, communication applications, housing, health, and hygiene are some examples of the usage of biorefinery products [67, 105]. Figure 2.11 presents the biorefinery products derived from biomass.

According to Figure 2.11, biomass is converted to biofuels, biochemicals, biomaterials, and biopower. Solid biofuels such as coke and lignin, liquid biofuels such as methanol, ethanol and biooil and gas biofuels such as methane, hydrogen, and syngas are the common biofuels derived from biomass in a biorefinery.

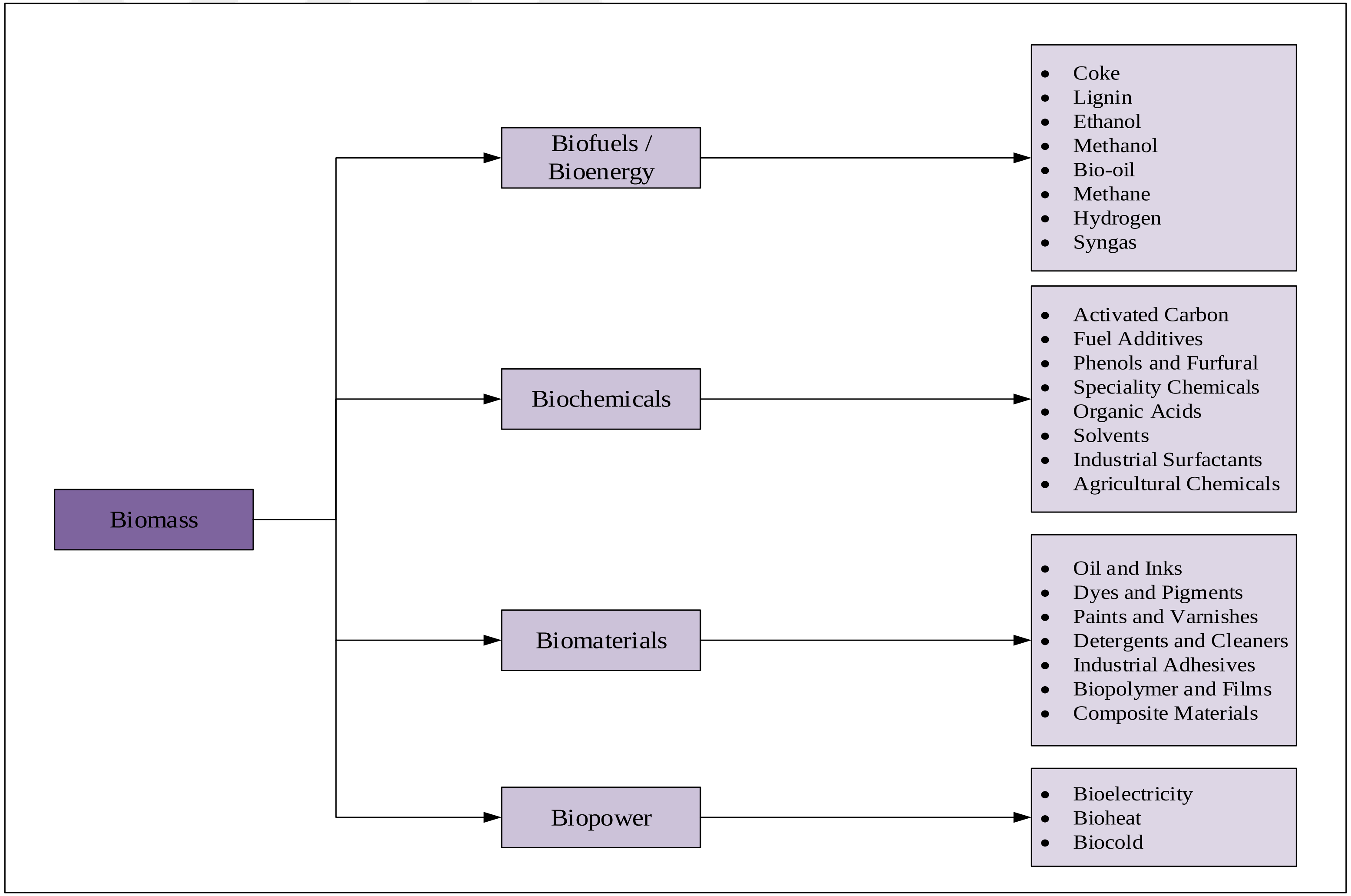


Figure 2.11 : General scheme of the bioproducts from biomass, adapted from [32].

Activated carbon, phenols, furfural, fuel additives, specialty chemicals, organic acids, solvents, surfactants, and agricultural chemicals are the main biochemicals and oil,inks, dyes, paints, coatings, varnishes, pigments, detergents, surface cleaners, adhesives, biopolymer, films, and composite materials are the best-known biomaterials [32].

2.5.1 Biofuels

Biofuels are produced from biomass through various pathways such as thermochemical conversion and biochemical conversion. The usage of biofuel instead of fossil fuel has several differences. First of all, while biofuels contain oxygen element, fossil fuel has an oxygen-free compound. One other main superiority of biofuels are containing lower sulfur and nitrogen level according to fossil fuels. The advantages of biofuels classified into economic advantages, environmental advantages and energy security. Economic growth sustainability, provide an opportunity of rural manufacturing jobs, the reduction of fossil dependency, development in agriculture, provide fuel diversity, expanding investing in plants and equipment are the economic impacts of biofuels. Reducing of GHG, air pollution, and carbon monoxide production, providing biodegradability, and increasing use of land and water, and carbon sequestration are the economic impacts of biofuels, and also, ready availability, domestic distribution, sustainability in international policies and renewability are the increase the energy security of biofuels [106]. The primary usage of biofuels is in the transportation sector. Then, industry, electricity generation, and house heating follow the transportation sector [107]. Biofuels, classified into two groups. Sugar and starch based plants are used to produce first generation biofuels, while second-generation biofuels are produced from lignocellulosic materials [108]. The main difference between the first and second generation biofuel is, second-generation biofuel does not compete with food and feed industry. Figure 2.12 shows the process chain of biofuel production.

2.5.1.1 Bioethanol

Bioethanol is the most commercialized biofuel in the world, recently [108]. Bioethanol is flammable, colorless liquid, soluble in water and used in different application areas such as transportation, medical and food industries. Bioethanol used as fuel, fuel additives or industrial chemical [110].

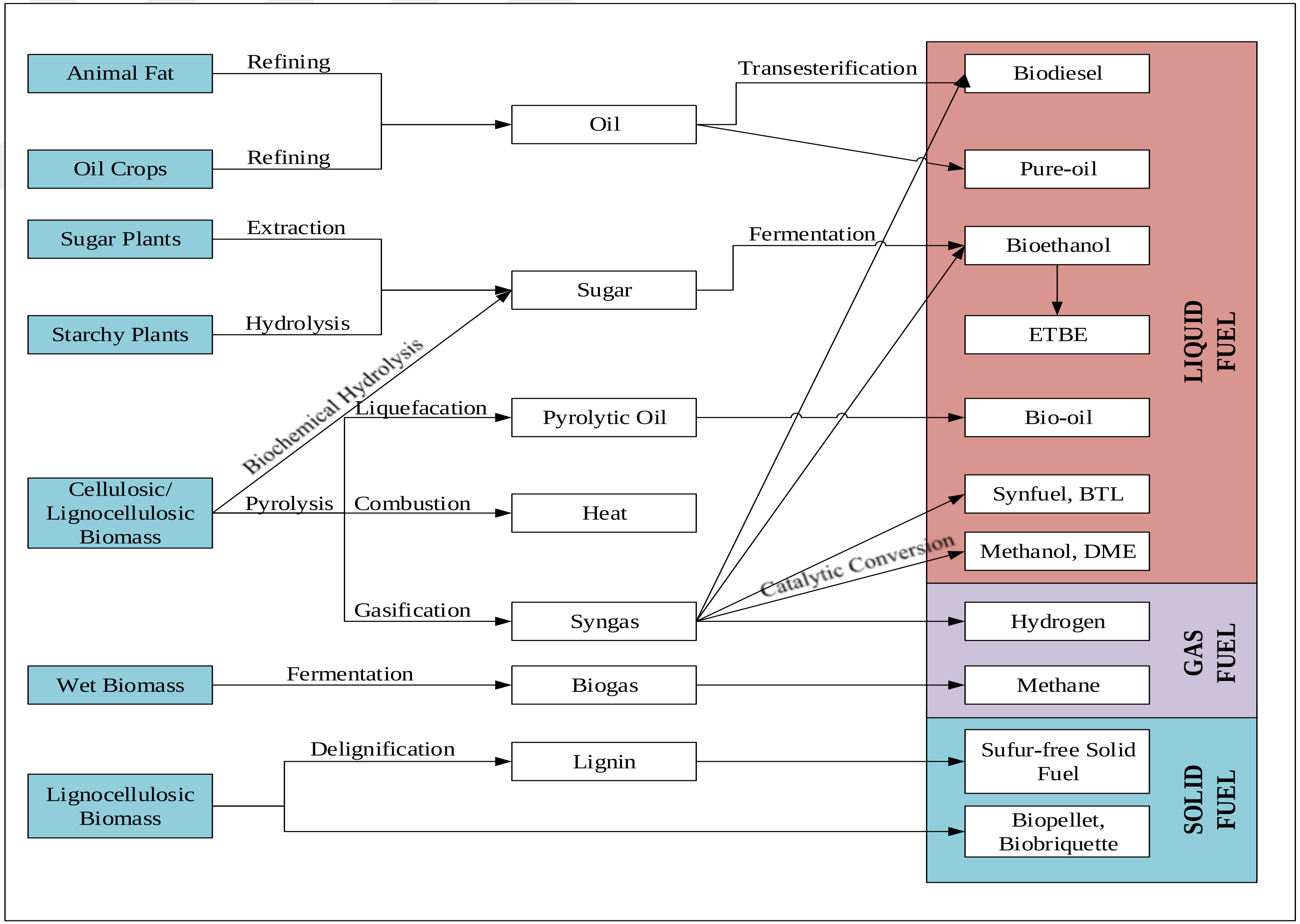


Figure 2.12 : Process chain for biofuel production, adapted from [109].

Bioethanol can be blend with any ratio of gasoline. Currently used ethanol blends for fuel usage are described below.

- E5: 5% of bioethanol is blended with 95% of gasoline
- E10 (Gasohol): 10% of bioethanol is blended with 90% of gasoline
- E25: 25% of bioethanol is blended with 75% of gasoline
- E70: 70% of bioethanol is blended with 30% of gasoline
- E85: 85% of bioethanol is blended with 15% of gasoline
- E95: 95% of bioethanol is blended with 5% of gasoline
- E100: Pure bioethanol
- E-Diesel (Diesohol): Diesel fuel that contains a maximum of 15 percent bioethanol

Additionally, bioethanol is used as an oxygenate additive in fossil fuels to increase octane number instead of methyl tertiary butyl ether (MTBE). MTBE has toxic effects on humans and impacts on soil and groundwater contamination. On the other, hand ethyl tertiary butyl ether (ETBE) is produced from bioethanol and can be used as an additive [12, 109]. The properties of bioethanol are presented in Table 2.5.

Table 2.5 : Properties of bioethanol [109].

Molecular formula	C_2H_5OH
Empirical formula	C_2H_6O
Molecular weight	46.07 g/mol
Density	0.789 g/cm^3
Phase	Liquid
Solubility in water	Fully miscible
Melting point	-114.3^{o}C
Boiling point	78.4^{o}C
Flashpoint	<21^{o}C
Viscosity	1.2 cP at 20^{o}C
Lower Heating Value (LHV)	26.8 MJ/kg

First generation bioethanol is produced from sugar based biomass extraction by fermentation, from starch based biomass by hydrolysis and second generation biofuel is produced from lignocellulosic biomass by hydrolysis. 6-carbon sugars (C6) and 5-carbon sugars (C5) are required for bioethanol production. The stoichiometric equations of producing bioethanol from C5 and C6 sugars are given below.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \tag{2.1}$$

$$3C_5H_{10}O_5 \rightarrow 5C_2H_5OH + 5CO_2 \tag{2.2}$$

Bioethanol production steps are defined; however, detailed information is given in Section 2.9.4.

- Physical/chemical pretreatment
- Saccharification and fermentation
- Distillation
- Dehydration / Purification

2.5.1.2 Biodiesel

Biodiesel is one of the most common fuel for transportation which used in diesel engines without any modification. Biodiesel can be used directly in traditional diesel engines instead of fossil based diesel fuel. The main difference of using biodiesel having higher viscosity and it causes fuel injection duration, pressures, and atomization of diesel injection engines [109]. Additionally, a higher flash point in biodiesel makes it non-flammable and nonexplosive in contrast to fossil diesel with the flashpoint 64ºC. Also, biodiesel is biodegradable, nontoxic and expressively decreases hazardous emissions on health and environment when combusted as a fuel [108]. Biodiesel can be used in diesel blend in engines. Typical blends are shown below.

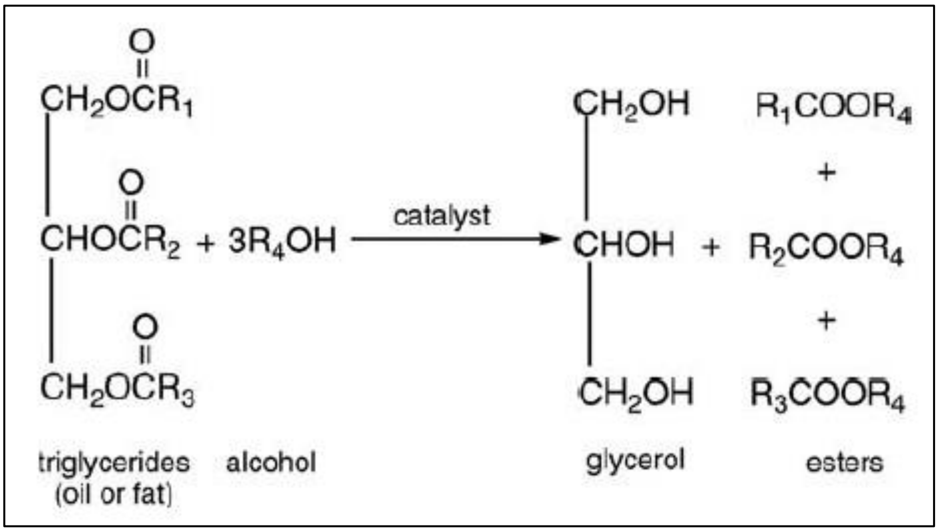
- B85: 85% of biodiesel is blended with 15% of fossil based diesel
- B95: 95% of biodiesel is blended with 5% of fossil based diesel
- B100: Pure biodiesel

The properties of biodiesel are shown in Table 2.6.

Table 2.6 : Properties of biodiesel [109].

Density	0.88 kg/L
Phase	Liquid
Viscosity	7.5 mm^2/s
Flashpoint	120ºC
Caloric value	37.1 MJ/kg at 20ºC

Biodiesel is produced from oil based plants such as vegetable oils, fats, greases, and wastes oils by a transesterification reaction with the aim of mainly basic catalyst [32]. Figure 2.13 presents the esterification reaction during biodiesel production.



$$CH_2OCOR_1 - CHOCOR_2 - CH_2OCOR_3 + 3R_4OH \xrightarrow{\text{catalyst}} CH_2OH - CHOH - CH_2OH + R_1COOR_4 + R_2COOR_4 + R_3COOR_4$$

Figure 2.13 : Transesterification reaction for producing biodiesel [108, 109].

In transesterification reaction, oil is reacted with alcohol that is mainly methanol or ethanol, and ester and glycerol are produced. If consumed alcohol is methanol, the produced ester is methyl ester while ethyl ester is produced when ethanol is used as alcohol. KOH or NaOH are used as a catalyst to increase the rate and yield of the reaction. Usage of excess solvent, move the equilibrium to the left side because of being a reversible reaction. Using basic catalyst in biodiesel production has high efficiency (98%) which requires low temperature and pressure [108].

2.5.1.3 Bio-oil

Bio-oil is the liquid biofuel that generated by biomass pyrolysis. Pyrolysis is the thermal decomposition reaction when oxygen deficiency exists. The absence of oxygen prevents biomass combustion in thermal conditions. Generally, the color of bio-oil is brown, dark red, or black and the density is 1.2 kg/l. The moisture content of bio-oil is in the range of 14-33% and conventional water separation methods such as distillation cannot apply smoothly. The higher heating value (HHV) of bio-oil is 15-22 MJ/kg, while fossil based fuel oil is 43-46 MJ/kg. The reason for the reduction of HHV is having a high ratio of oxygenated compounds [108, 111]. Manufactured gas, biodiesel, or biomethane can be produced from bio-oil by gasification or other methods. Additionally, bio-oil is soluble in alcohol. Thus, blending with alcohol decreases viscosity, increases fuel stability and fuel properties. On the other hand, the content of bio-oil depends on the content of the feedstock, reactor and reaction parameters [110, 111].

2.5.1.4 Biogas

Biogas is a gas mixture which contains methane (50-60%), carbon dioxide (35-40%) and trace amounts of hydrogen, nitrogen, hydrogen sulfide and produced by anaerobic digestion from manure, agricultural crop residues, food and feed process residues, and dedicated energy crops with the aid of microorganisms. The application areas of biogas are internal combustion engines and heat and power production [112].

The digestion process occurs in the absence of air. The digestion process includes four main steps. The first step of biogas production is hydrolysis, and in this step, complex organic matters such as polysaccharides and fats are converting to degraded organic matters such as carbohydrate, proteins, and lipids by hydrolytic bacteria. Next, monomeric organic matters such as sugars, amino acids, and fatty acids are produced by acidogenic bacteria. Then, the fermentation step occurs by acidogenesis bacteria, and intermediary compounds (alcohols, long-chain fatty acids), acetate, hydrogen, carbon dioxide are produced. At the last step, acetate, hydrogen, carbon dioxide are converted biogas by methanogenesis bacteria [109, 110].

The purification step is required for using biogas applications. Combustion of biogas in internal combustion engines produces lower gas emissions than petrol and diesel alternatives. The comparison of emissions reduction with petroleum and diesel alternatives are presented in Table 2.7.

Table 2.7 : Comparison of toxic emission reduction of biogas, petroleum, and diesel [109].

Emissions	Petroleum	Diesel
NO_x	55%	80%
CO	55%	50%
Particulate Matter	na	98%
Hydrocarbons	80%	80%
Ozone Formation	65%	85%

2.5.1.5 Biohydrogen

Biohydrogen is a secondary product compared to other biofuels. Hydrogen is non-toxic compound, and combustion gases are only water and small amounts of nitride hydrogen. A small amount of nitride hydrogen has no significant impact on the environment. Therefore, biohydrogen is accepted that the cleanest biofuel. Following nuclear energy, biohydrogen is in the second place due to HHV. If the comparison is made between biohydrogen and gasoline, HHV of biohydrogen is 28900 kcal/kg while

HHV of gasoline is 10848 kcal/kg. Engine fuel, chemical raw materials, fuel cell fuel, structural materials are some examples of hydrogen application. Major technological modifications are not required to use biohydrogen instead of fossil fuels. However, minor modifications are required for internal engine usage [113, 114]. Biomass gasification and microbial metabolism are two main hydrogen production methods. On biomass gasification method, biomass is converted to the combustible gas mixture which contains carbon monoxide (CO), hydrogen (H_2), and a trace amount of methane (CH_4) with the thermochemical conversion. The main biomass gasification reaction steps are described below [114-116];

1. Thermal decomposition: Biomass is converted three-phase product such as gas, coke and first tar.
2. Pyrolysis: Secondary and tertiary tar is produced from first tar.
3. Gas formation: Gasification reaction contains both homogeneous and heterogeneous gas formation reactions through pyrolysis and coke combustion.

Oxygen, air or steam is required for gasification. While combustion requires adequate oxygen to fully biomass combustion, oxygen demand in the gasification reaction is only as demands of a thermal chemical reaction. The main technical challenge of biohydrogen production is the purification of hydrogen. High-quality pieces of equipment are required for purification. Additionally, to commercialize biohydrogen production, hydrogen production efficiency has to be increased [114].

One other hydrogen production method is using microbial metabolism. Hydrogen production method utilizing microbial metabolism has low impacts on the environment, requires energy saving and energy recovery from wastes [114].

2.5.1.6 Biopellet and biobriquette

Biopellet and biobriquette are fundamentals solid biofuels and produced from lignocellulosic biomass. The aim of production of biopellet and biobriquette is producing high calorific value fuels with lower volume. The structure of lignocellulosic biomass is heterogeneous and ununiform. Hence, storage, transportation of lignocellulosic biomass constitute problems. Usage of lignocellulosic biomass in biopellet and biobriquette production solve transportation and storage problems. The advantages of biopellets and biobriquettes have lower moisture content cause higher calorific value; higher density reduces transportation costs, uniform size and shapes cause easiness in storage and reduce storage costs [110]. The main difference between biopellet and biobriquette is the size and dimensions of fuel. The dimensions of the biopellet are mainly 5-12 mm diameter and 10-30 mm length, and the shape is a cylinder. The dimensions of biobriquette are 30 mm×30 mm for square area and 30-80 mm length [117].

2.5.1.7 Sulfur-free solid fuel

The sulfur-free solid which is also known wood powder is used for industrial scale combustion plant to generate heat. Biomass feedstock contains lower sulfur content than fossil based feedstock; the sulfur content of combustion gases are lower than fossil based alternatives. Sawdust, bark or shavings are used as feedstock of sulfur-free solid fuel. When the production of sulfur-free solid fuel, the lignocellulosic feedstock is crushed, dried and milled and converted into very fine particles. The aim of the usage of sulfur-free solid biofuel is increasing surface area and causes high-efficiency dıuring combustion. The primary disadvantage of sulfur-free solid fuel is dust explosions. Hence, from production to combustion, sulfur-free solid biofuel is stored in closed-loop systems for security. The physical properties of sulfur-free solid fuel depend on the feedstock type and milling parameters [110].

2.5.2 Biochemicals

Currently, a large number of industrial chemicals are derived from petroleum. However, these chemicals can also be formed by conversion of biomass. Biological and chemical processes are required to produce high value-added biochemicals from biomass [112].

Figure 2.14 presents a general scheme of biochemicals from biomass. Some examples of biochemicals are gallic acid, ferulic acid, coumaric alcohol, mixed and higher alcohols, acetone, glycerol, lactic acid, 3-hydroxypropionate, succinic acid, aspartic acid, furfural, levulinic acid, itaconic acid, xylitol, 5-hydroxymethylfurfural (HMF), gluconic acid, sorbitol, citric acid, and acetic acid. The attention of biochemical production is developing. According to forecasting reports, the market share of biochemicals will expand from 2% to 22% by 2025 [105, 118].

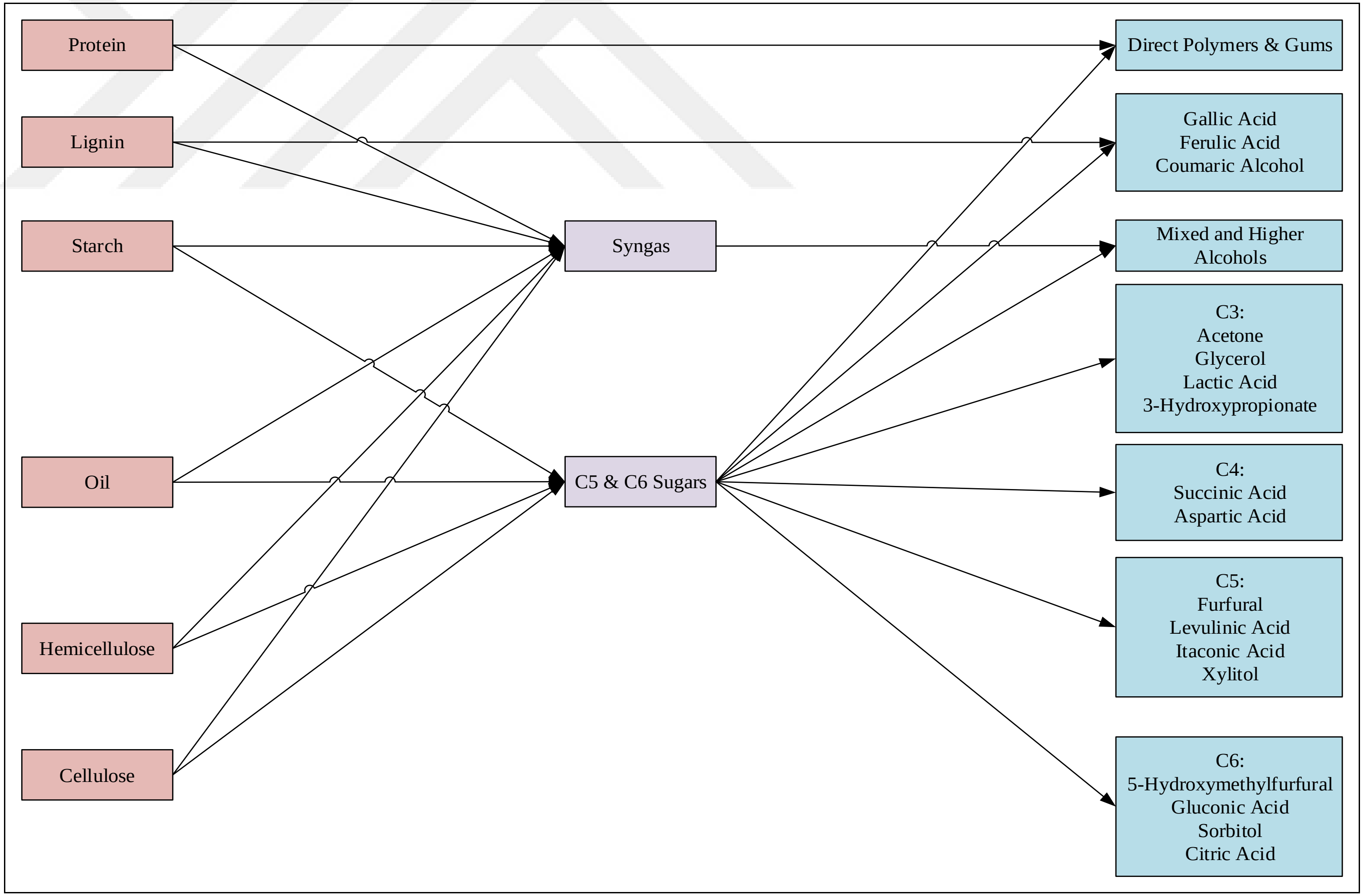


Figure 2.14 : The general scheme of biochemicals from biomass, adapted from [67, 105].

2.5.2.1 Furfural

According to Pacific Northwest National Laboratory (PNNL), National Renewable Energy Laboratories (NREL) and US Department of Energy (US DOE), furfural is selected as one of the top 30 platform chemicals which derives from biomass [119]. The molecular formula of furfural is C_4H_3OCHO and firstly, J.W Döbereiner isolated furfural in 1832. Furfural has been producing in industrial scale since 1922 [120]. Figure 2.15 presents the molecular structure of furfural.

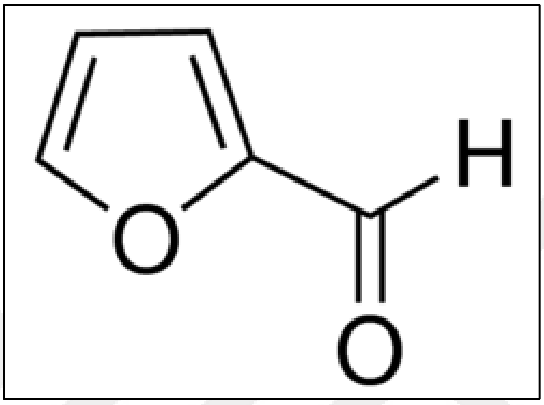


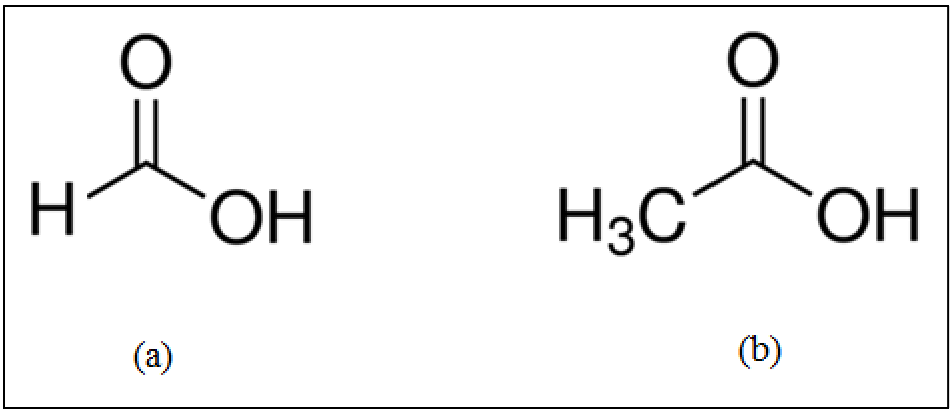
Figure 2.15 : Molecular structure of furfural.

Furfural is produced by natural dehydration of xylose which is a monosaccharide that found in hemicellulose fraction of lignocellulosic biomass. Theoretically, biomass that contains 5C sugars such as xylose and arabinose will become a raw material to the production of furfural [121]. Strong acid catalyst addition improves furfural yield 70-85% [122, 123]. Furfural is also an intermediate chemical to produce furan based chemicals and solvents [124-129]. Furfural are used as selective extraction agent, solvent, transportation fuel, gasoline additive, lubricant, decolorizing agent, agent for vulcanization, nematicide and fungicide, a flavoring agent in food and beverage industry, component of industrial herbicides, insect repellent, pesticides, antiseptics, disinfectors, and corrosion removers, resins, cleaner, detergents and an intermediate matter in the synthesis of pharmaceuticals, chemicals and biopolymers [120, 130, 131]. The technological improvements are required for effective furfural production to compete with petroleum based products.

2.5.2.2 Formic acid and acetic acid

Formic acid and acetic acid are the main platform chemicals derived from biomass. The molecular formula of formic acid is CH_2O_2, and acetic acid is CH_3COOH.

Molecular weight is 46.03 g/mol and 60.05 g/mol for formic acid and acetic acid, respectively. The molecular structure of formic acid and acetic acid are presented in Figure 2.16.



(a) (b)

Figure 2.16 : Molecular structure of (a) Formic acid and (b) Acetic acid.

The usage of formic acid is available in textile, leather, pharmaceutical, rubber and chemical industries. Also, formic acid has great potential to use in fuel cells and hydrogen storage [132-135]. Thermal cracking and catalyst addition are used for formic acid production [136]. Recently, H_2SO_4 is selected as an efficient catalyst for formic acid production from biomass [137]. On the other hand, during different chemical productions such as levulinic acid, sorbitol, ethylene glycol, 5-HMF, lactic acid, glycolic acid and gluconic acid, formic acid is produced as a by-product [138-145].

Acetic acid is colorless and corrosive with pungent smell [146]. Widely application area exists in the chemical industry for acetic acid. Both synthetically and by bacterial fermentation are used for acetic acid production. Synthetical production of acetic acid is mainly derived from petroleum based materials and includes 90% of total acetic acid production [147]. Acetic acid produced by anaerobic homoacetogens and aerobic acetic acid bacteria. Liquid-liquid extraction, adsorption, precipitation, distillation, reactive distillation or membrane process are required for acetic acid purification [146]. The usage of acetic acid is available in chemical, textile, leather, pharmaceutical, rubber and other industries [132].

2.5.2.3 5-HMF

5-HMF is furfural derived compound, and it is a value-added chemical for the industry. A method of 5-HMF synthesis was firstly published in the literature by Düll and

Kiermeyer in 1895. They made different studies and published in the same year. Since that time lots of studies have been published about 5-HMF synthesis [148, 149]. The molecular formula is $C_6H_6O_3$, and the molecular weight is 126.11 g/mol. Figure 2.17 shows the molecular structure of 5-HMF.

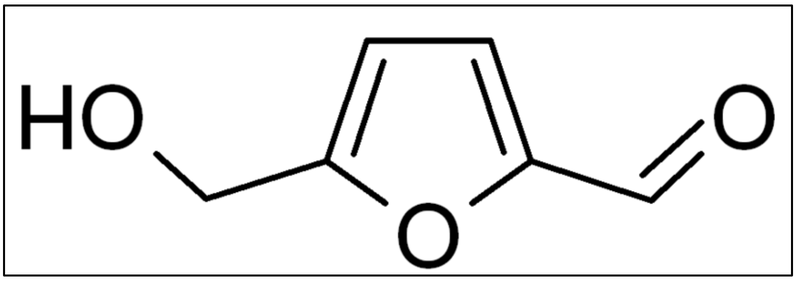


Figure 2.17 : Molecular structure of 5-HMF.

The synthesis of 5-HMF occurs during dehydration of 6C sugars with lost three water molecules. Also, additional catalysts such as organic acids, inorganic acids, salts, Lewis acids, and others are used for increasing the production yield of 5-HMF [150]. The main problem for 5-HMF production is recovery 5-HMF in aqueous solution. Distribution coefficient between the phases is not convenient. However, an organic solvent such as methyl isobutyl ketone, ethyl acetate, diethyl ether and acetone usage as an extractive agent defeats this problem [151, 152]. 5-HMF is used as an intermediate molecule for both biofuel production such as dimethylfuran and biochemical production [148].

2.5.2.4 Levulinic acid

Levulinic acid is one of the biochemical that produced in biorefineries by lignocellulosic biomass and defined as one of the top 30 platform chemicals which derives from biomass [119]. The first study was published in the 1870s, then specific potential application of levulinic acid review was published in 1956 [153]. The potential of levulinic acid is increasing due to having variety in applications different industries [154]. The molecular formula of levulinic acid is $C_5H_8O_3$ and molecular weight is 116.11 g/mol. The molecular structure of levulinic acid is presented in Figure 2.18.

Levulinic acid is produced during the hydrolysis of hydrocarbons. Mineral acid addition as catalsyt is increased the levulinic acid yield. Different conversion methods to degrade levulinic acid to other liquid biofuels are applicable [155]. Currently, the

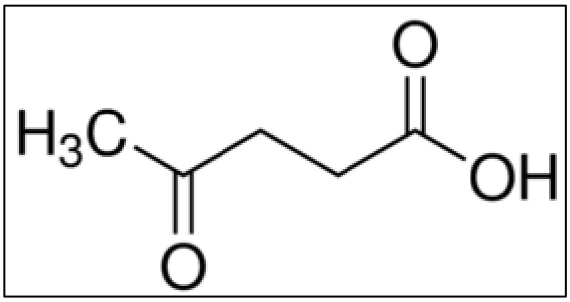


Figure 2.18 : The molecular structure of levulinic acid.

application of levulinic acid is available in coatings, polymers, printing, biologically active material, lubricants, adsorbents, electronics, photography, battery, personal care product industry [156-162].

2.5.3 Biomaterials

Biomaterials are one of the main product of biorefineries. Biomaterials have large application areas in the industry. The primary importance of biomaterials is replacing fossil-derived materials. Therefore, increasing environmental awareness, make biomaterials more crucial. Bioplastics, biofoams, biorubbers, biocomposites, biopolymers, biolubricants, biosolvents, biosurfactants, enzymes, biopharmaceuticals, bioprinting inks, paints and surface coatings, wood and natural fibers, epoxy resin, and phenolic resin are some examples of biomaterials [32, 107, 111, 112, 163-168]. The market share of biomaterials in the biochemical market was 20.9% in 2010, and according to forecasting reports, it will increase by 32.5% [165]. Research and developments still require for commercializing biomaterials.

2.5.4 Biopower and bioheat

Biopower (bioelectricity) and bioheat are products of biorefineries. These products generally can be used biorefineries own demand. Surplus biopower and bioheat are sold to markets or fed into the grid. Concurrent production of biopower and bioheat from a single feedstock such as natural gas, oil, coal, or biomass (woody) is referred to as cogeneration [169]. In biomass concept, wood chips are used in cogeneration plants [170]. Heat and power generation can be done with the use of a steam, gas or a combined both steam and gas turbine cycle. In the steam turbine cycle, combusted fuel is utilized to produce gases with high temperature. Steam is generated by high temperature. A turbine and an electric generator are found in this cycle to produce biopower. Next, bioheat is produced by the residual stream. In the gas turbine cycle, biopower is generated by combusted gas expansion in the turbine. Rest of gas is used to bioheat production. In the combination of both steam and gas cycle, biopower is generated by expansion of high temperature combusted gas and then, bioheat is produced by the rest of steam. Steam turbine cycle is the most widely used technology in cogeneration types [171].

2.6 Biorefinery Classifications

Different definitions are used for biorefineries. The US DOE defined biorefinery as “A plant that includes biochemical and thermochemical processes and conversion from biomass into value-added products exists. These products can varied from biomaterials to biofuels. Mechanical, thermal, chemical, and biochemical processes are using in biorefineries.” [91]. The NREL defined biorefinery as “A biorefinery is a plant that includes the processes and equipment which requires for biomass conversion to produce biofuels, biopower, and biochemicals which derived from biomass. The biorefinery concept is parallel to current petroleum refineries. Commercial biorefineries have been defined as the most favourable pathway to the develop of a local biobased industry” [92]. IEA has defined biorefineries as “Biorefinery includes sustainable processes to conversion of biomass into a large variety of bioproducts and bioenergy” at Bioenergy Task 42 on Biorefineries [29].

Technological classifications consist of three main groups such as first generation, second generation, and third generation biorefineries. First generation biorefineries are also known as conventional biorefineries, uses grain feedstock, and has a fixed processing capability. It does not permit any alteration, and this type can be used for comparison purposes only. Second generation biorefineries use grain feedstock and have the ability to generate different types of end-products. Second generation biorefineries are more flexible than first generation biorefineries and today’s technology is often used second generation biorefineries. Third generation (advanced) biorefineries convert agricultural or forest biomass to different products with multiple streams. However, third-generation biorefineries are not commercially fully developed yet [31].

According to IEA Task 42, the classification of biorefineries depends on four main classes. These are platform based biorefineries, product based biorefineries, feedstock based biorefineries, and processes based biorefineries. Platforms are links between feedstocks and final products, and their concepts are similar to fossil-based refineries. Firstly, biomass is converted to intermediated. Then, these intermediates are converted to bioenergy and/or chemical products and named as sugar based biorefinery, starch-based biorefinery, lignocellulose-based biorefinery, and green biorefinery, vegetable oil and marine biorefinery, synthesis gas biorefinery, and biogas biorefinery. For classification according to products approach, biorefineries can be divided into two main groups such as energy-driven and material-driven biorefinery systems. In energy-driven biorefinery systems, biomass is used for feedstock and second energy carriers such as transportation fuel, power and heat are produced. In material-driven biorefinery systems, biobased products are produced. According to feedstock classification approach, renewable carbon are obtained from various sectors such agriculture, forestry, industry & domestic activities and aquaculture. The last classification method is according to the process of biorefineries. Main process groups are mechanical, physical, biochemical, chemical, and thermochemical processes. All these processes require auxiliary energy and materials. According to Cherubini's classification method, platforms are the main priority for classification and platforms should be determined first. Platforms are named as one platform, two platforms or four platforms, etc. and these platforms could include both only one platform or combined more than one platforms [30, 103]. One other classification according to feedstocks is named as LCF, whole crop biorefinery, marine biorefineries, green biorefineries and the biorefinery two platforms concept [32].

2.6.1 Lignocellulosic feedstock biorefineries

LCF is the biorefineries that used lignocellulosic biomass as feedstock. Straw, reed, grass, wood, paper waste, etc. are examples of lignocellulosic biomass. The main advantages of LCF biorefineries are largely biomass variety, and lignocellulosic biomass is not compete with food industry. The lignocellulosic biomass contains cellulose, hemicellulose, and lignin structure. Due to the recalcitrant structure of lignocellulosic biomass, pretreatment methods should be applied in LCF biorefineries. In LCF biorefineries, lignocellulosic biomass is converted biofuel, biochemical, biomaterial, biopower and bioheat with thermochemical and biochemical conversion [32]. The detailed information is given in Section 2.7.

2.6.2 Whole crop biorefinery

Whole crop biorefinery feedstocks are rye, wheat, triticale, and maize. The primary specialty of whole crop biorefineries is using feedstock with both straw and seed parts. The first step of whole crop biorefinery is a mechanical separation of feedstock and separate seed and straw part. Straw consists of chaff, nodes, ears, and leaves. Straw part can be used to produce electricity by combustion and converted to syngas by gasification. Also, straw is separated to its composition components such as lignin, hemicellulose, and cellulose and can be used in sugar platform biorefineries. Seed can be used both as food or feed by grinding or converted to starch. After biological conversion, starch is converted to glucose and ethanol can be produced from glucose. Also after chemical conversion, syngas, methanol, polyhydroxybutyrate (PHB), sorbitol, glucosamine, acetate based starch, and carboxymethyl starch can be produced from starch. On the other hand, bioplastics, co- and mix-polymerizates, binders, adhesives, and cement will be products of whole crop biorefineries [33, 172]. In whole crop biorefineries, natural structures and structural components are converted by high known fundamental technology, and these technologies can be still functioning. However, high feedstock cost is a disadvantage of whole crop biorefineries [32].

2.6.3 Green biorefinery

The feedstock of green biorefineries is mostly green or wet crops such as grass, lucerne, alfalfa, herbs, etc. The benefits of the green biorefineries are excessive biomass yield, well pairing with agricultural processes and reduce cost of the feedstocks. At green biorefineries, raw green biomass is sent to the drying section. Then, green crops are pressed, press juice and press cake are separated. Green pellets for fodder and solid fuel, raw materials for syngas, hydrocarbons, biogas, fibers, fleece, and chemicals can be produced from press cake. Also, acids such as lactic acid, amino acids, organic acids, and its derivatives, proteins, enzymes, and ethanol can be produced from press juice [32].

2.6.4 Marine biorefinery

In the aquatic system, biomass diversity as extensive as in terrestrial systems. The interest of biomass in mainly on terrestrial systems, currently. Therefore, aquatic system biomass is not gain deserved attention. Aquatic system biomass contains microalgae, macroalgae and their derived products. Microalgae consist of green, golden, and blue/green algae and are the phytoplankton life form, and possibly generate the highest biomass potential in the world. Algae contain important quantity of oils and carbohydrates. They contain also vitamins due to species and life conditions [34]. Micro and macroalgae (seaweeds) are used in marine biorefineries and divided two main subgroups such as microalgae biorefineries and seaweeds biorefineries [173]. The main product of marine biorefineries is biofuel. However, technological developments are required to commercialize of marine biorefineries [34].

2.6.5 Two-platform concept biorefineries

Two-platform concept biorefineries almost consist of sugar platform and syngas platform. Biochemical conversion is a fundamental process for sugar platform, and thermochemical conversion and gasification are fundamental processes for syngas platform. Also, thermal and thermochemical conversion methods can be found in syngas platform processes. According to the moisture content of biomass, the application of the process is determined [174]. The main advantage of this type of biorefineries is the production of bioenergy, biofuels and biomaterials with slightly complex and low technology [32].

2.6.6 Integrated biorefinery

In the 1980s, a new approach had been developed in chemical engineering to use energy more efficiently. That was called process integration. Process integration is more effective in a complex process than standalone units [52]. The process which contains process integration is called integrated process. The biorefinery which has process integration is also named as an integrated biorefinery.

The integrated biorefineries are similar to biorefineries. Both, they produce biofuel, biochemicals, and biomaterials for optimizing feedstock usage and production costs. More research, development, demonstration, and reduction of production cost have to be required to compete with fossil fuels [53]. Integrated biorefineries contain one or more integration such as feedstock or product integration, heat integration, power integration, water integration, infrastructure integration, process synthesis, LCA, sensitivity analysis, uncertainty analysis, supply chain and the strategic planning [175, 176].

Computer-aided simulation is one of the most crucial process integration tool for both process synthesis and optimization. Figure 2.19 presents the difference in process design and integrated process design.

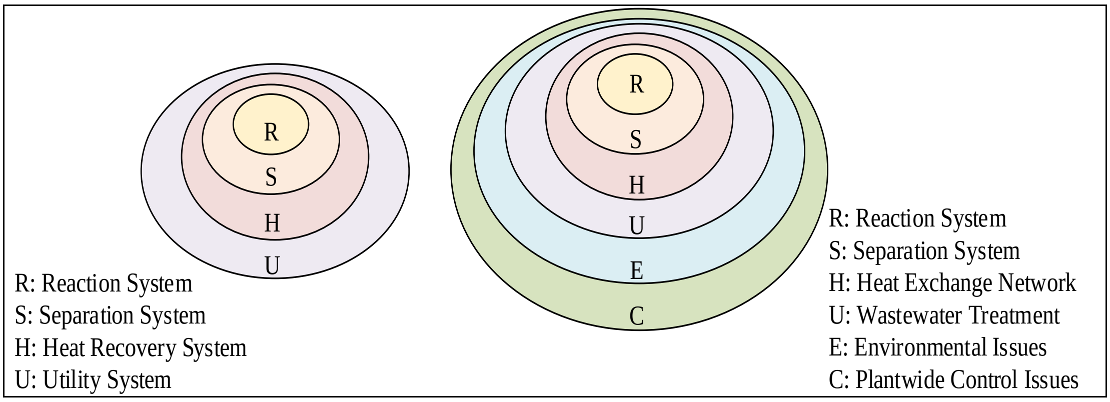


Figure 2.19 : Onion diagram of process design and integrated process design approaches, adapted from [52].

As it is seen in Figure 2.19, while process design contains systems such as reaction, separation, heat recovery and utility, integrated process design contains systems such as reaction, separation, heat exchange network, wastewater treatment, and issues such as environmental and plantwide control. Therefore, for simulating integrated biorefinery, heat exchanger network, wastewater treatment, environmental issues, and plantwide control systems have to be determined.

2.7 Lignocellulosic Feedstock Biorefineries

Lignocellulosic feedstocks are inexpensive and have high availability in the world. Figure 2.20 indicates the flow scheme of lignocellulosic feedstock biorefineries.

It is seen in *Figure 2.20* that, lignocellulosic biomass contains lignin, hemicellulose and mainly cellulose component. Lignin is used as a feedstock for the production of natural binder, adhesives, sub-bituminous coal and solid fuel which contains no sulfur. Hemicellulose can be converted to end-products such as furfural, thickeners, adhesives, emulsifiers, stabilizers, etc. and cellulose conversion causes fuel formation such as ethanol, an organic acid such as lactic acid and solvents such as acetone and butanol [32].

For designing third generation lignocellulosic biorefineries, main and co-products are varied according to design parameters. Thus, first of all, targeted products are well

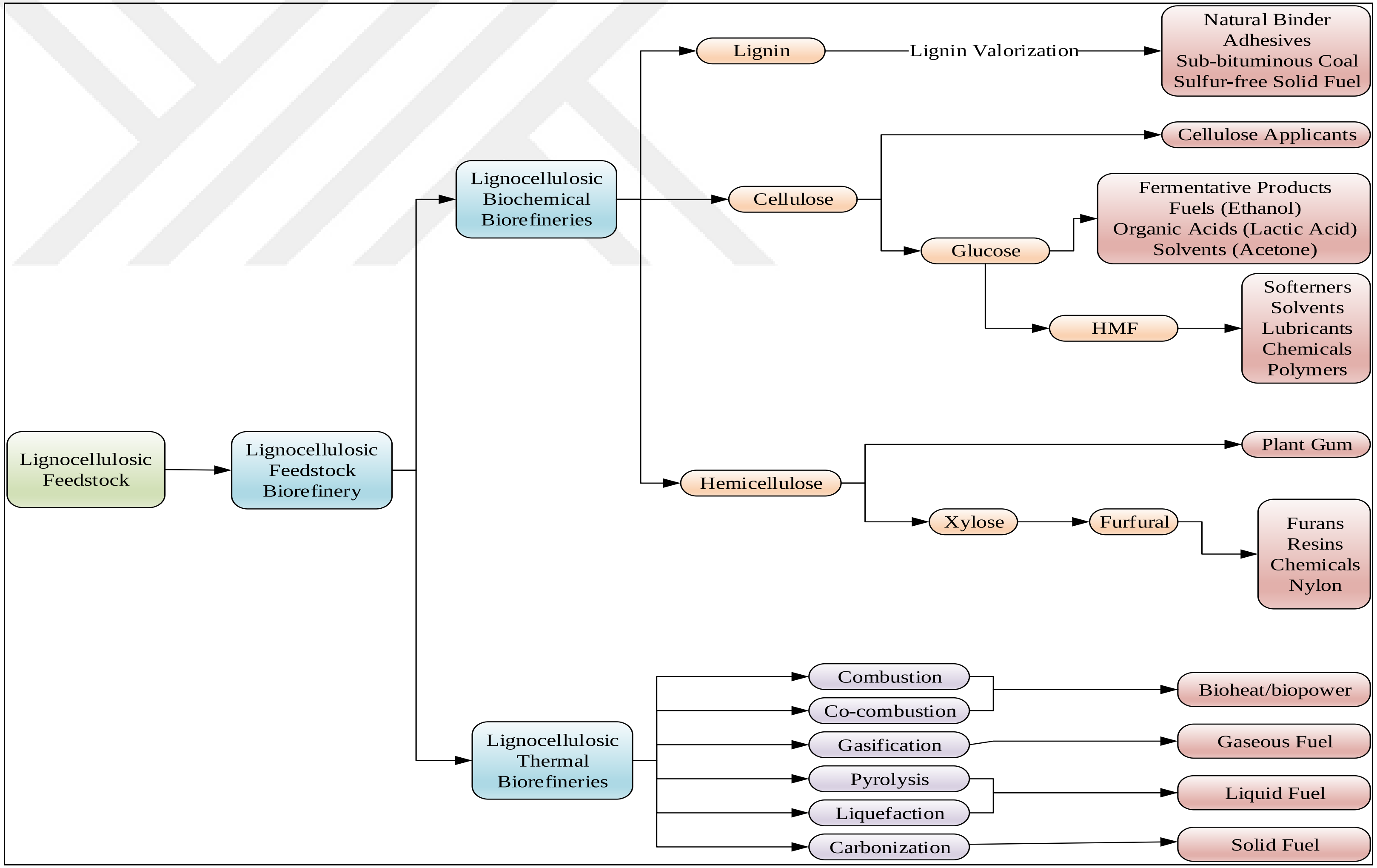


Figure 2.20 : General scheme of lignocellulosic feedstock biorefineries, adapted from [33, 177].

defined. Therefore, suitable pretreatment methods should be applied to lignocellulosic feedstock.

2.8 Lignocellulosic Feedstock Biorefinery Pretreatment Methods

In traditional first generation biorefineries from the sugary and starchy feedstock, microorganisms are used to convert directly to ethanol from sugar. However, for lignocellulosic biorefineries, pretreatment is necessary for converting lignocellulosic polymer structure to monomer structure for increasing yield [1].

The chemical and physical barriers for biofuel production are complex structure of lignocellulosic feedstock causes difficult hydrolysis, the mixture of pentose and hexose sugars causes fermentation problems because either different enzymes are needed for fermentation or pentose sugars are not readily fermented and unwanted products such as extractives, by-products causes inhibitory effects on hydrolysis and fermentation [69, 178 - 181].

The main aims of pretreatment are broken down the lignin structure, decrease cellulose crystallinity, cause higher porosity or available surface area, separation of lignin from carbohydrate structure, and increase digestibility of cellulose and must be cost-efficient [37, 69]. Hence, the enzyme accessibility is increased [182]. On the other hand, pretreatment have to prevent the degradation or reduction of carbohydrate and production of byproducts which act as an inhibitor at enzymatic processes [183]. The pretreatment cost is one of the most expensive processes in lignocellulosic biorefineries. However, it highly improves conversion efficiency [184]. Previous studies show that pretreatment is increased sugar yield higher than 90% [182].

Pretreatment methods of lignocellulosic biomass can be separated into four main categories such as physical pretreatment, chemical pretreatment, biological pretreatment, and physicochemical pretreatment methods [37, 181, 182].

2.8.1 Physical pretreatment

Physical pretreatment methods contain mechanical treatment and pyrolysis methods. The primary goals of physical pretreatment are to increased the reachable surface area and expanded pore size of lignocellulosic feedstocks and reduce the crystalline structure and degree of cellulose polymerization [178].

For decreasing the crystallinity of lignocellulosic biomass, chipping, grinding and milling methods are applied. The size of pretreated biomass is reduced to 1-3 cm after chipping and 0.02-0.2 cm after milling or grinding treatment processes [37, 183]. Different types of milling process can be applied for lignocellulosic biomass. The types of milling process are vibratory, ball, disk, and hammer to enhance enzymatic hydrolysis [185]. If the milling processes are comparing, the efficiency of vibratory milling is more than simple ball milling for decreasign crystalline structure of cellulose, and the efficiency of disk milling is more than hammer milling because of producing fibers instead of finer bundles [186]. Mechanical comminution is a high energy consuming process, and hardwood requires more energy than agricultural residues. Then, the choices of mechanical comminution are well assessed according to the type of lignocellulosic biomass [187]. Different studies show that, although mechanical comminution improves yield, it is not applied individually for lignocellulosic biomass. Especially, applying chemical pretreatments after mechanical comminution decreases consumption of energy, cost of solid-liquid fraction separation and do not cause high inhibitory products [186, 188].

Another physical pretreatment method is pyrolysis. When the temperature is 300°C and above, cellulose fastly breaks down to generate gaseous and solid products such as char [183]. The break down rate is getting later at lower temperatures. Pyrolysis process is dveloped in the presence of the oxygen [189].

2.8.2 Physicochemical pretreatments

Physicochemical pretreatment is combined both physical and chemical pretreatment method to improve sugar yield efficiency, provide increased transportability for enzymes into the cellulose [190]. Physicochemical pretreatment methods include steam explosion, ammonia fiber explosion (AFEX), CO_2 explosion, liquid hot water treatment (LHW) and microwave irradiation. These types of pretreatments are selected depend on process conditions and the chemical and physical structure of biomass [178].

2.8.2.1 Steam explosion

Steam explosion method is extensively applied pretreatment methods which includes both chemical and physical methods to explode the crystallinity form of biomass [182]. In this method, lignocellulosic biomass is subjected to increased pressure up to 4.83

MPa saturated steams at high temperature up to 260°C, and retention time is varied from several seconds to several minutes. Then, the sudden pressure reduction to atmospheric pressure is existed [37, 179]. The explosion with high pressurized steam decompression of biomass breaks the strong structure of biomass [181]. The rapid pressure reduction causes to splitting the cellulose bunches to provide the reachability for enzymatic reactions on bioethanol production steps [191]. The main significant property of steam explosion method is steam applied directly on lignocellulosic biomass, and no other chemicals are added [179]. Steam explosion has reduced environmental effects, low hazardous process chemicals generation and high energy efficient pretreatment method [184]. Also, operation cost is reduced for less enzyme usage. However, equipment must be secure for high pressure and rapid pressure drop, then the cost of equipment is increased for steam explosion pretreatment [192]. Studies show that, steam explosion treated poplar chips have 90% efficiency after 24 h enzymatic hydrolysis, while untreated poplar chips have only 15% efficiency [193].

2.8.2.2 Ammonia fiber explosion

AFEX pretreatment method is an alkaline method and in this pretreatment method lignocellulosic biomass pretreatment is actualized with ammonia in liquid form at excess temperature and pressure; next, the pressure rapidly is released to atmospheric pressure [183]. Generally, the pretreatment conditions are set as 1 to 2 kg of ammonia per kg of dry biomass of the ammonia loading; 60°C-120°C of temperature, 1.72-2.06 MPa of pressure and 10 minutes of retention time [37]. Likely to steam explosion pretreatment method. However, ammonia in liquid form is consumed instead of water in AFEX method [1]. Also, temperature is significantly lower than steam explosion and causes reduction of energy consumption and lower overall cost [182].

The AFEX pretreatment has been used for different lignocellulosic biomass such as alfalfa, wheat straw and wheat chaff [194]. However, it is not efficient on lignocellulosic biomass which includes high lignin ratios [195]. The parameters which affect the AFEX pretreatment method are ammonia ratio, pressure, temperature, water ratio, pressure discharge, releasing time [196]. The effect of alkali agent and high pressure causes a physicochemical variation in the lignocellulosic biomass structure, decrystallization of cellulose and explode the linkages between lignin and carbohydrate [1, 178, 197]. It was reported that, after AFEX pretreatment of bermudagrass at 100°C for 30 min, the sugar yield was found as 94.8% [198].

AFEX has several benefits such as environmentally friendly, higher energy efficiency, mild reaction conditions, does not produce any inhibitory or toxic materials, does not demand to the decreasing size of particle and nitrogen source, and produce negligible of inhibitors [178, 179, 197, 199]. On the other hand, using a high amount of ammonium causes high energy consumption for ammonium recovery and recycling and requires a high cost for practical applications [1].

2.8.2.3 Ammonia recycle percolation

Ammonia recycle percolation (ARP) method is similar to AFEX method, and some researchers accepted that both ARP and AFEX pretreatment method are the same. However, they have different characteristics [182]. In ARP pretreatment method, aqueous ammonia (2.5-15%) is used to biomass pretreatment which flow rate is 5 ml/min, with a temperature range is 140°C-210°C and the retention time is 90 minutes [200]. In ARP, the ammonia is recovered and reused, and aqueous ammonia acts with lignin and causes break down of lignin. Also, no inhibitory product is produced in ARP method. Hence, there is not water washing needed [37, 194]. ARP pretreatment method is found sufficient for delignification of hardwoods and herbaceous plants; however, for softwoods, the effectiveness is low.

2.8.2.4 Carbon dioxide explosion

Carbon dioxide explosion is a physicochemical pretreatment method and similar to the steam explosion and AFEX. However, CO_2 explosion needs a milder temperature than steam explosion and a decreased cost,while comparing with AFEX [37]. Zheng et al. indicated that CO_2 explosion pretreatment is required lower cost than steam explosion and AFEX [201]. Using CO_2 as a supercritical fluid with high pressure causes sufficient solubility of lignin [202]. The critical temperature (T_c) and critical pressure (P_c) of CO_2 is 31°C and 7.4 MPa, respectively. Supercritical CO_2 has significant potential for lignocellulosic biomass pretreatment [182]. At high pressure, CO_2 difuses the lignocellulosic biomass structure and increase its digestibility. When CO_2 collapses in water, it produces carbonic acid and improves the hydrolysis of hemicellulose as well as cellulose. Sudden pressure drop to gas in digester causes destroy of the biomass structure, and increase surface area and improves enzyme accessibility [203]. A raise in pressure causes rapid diffusion of CO_2 molecules into structure of the crystalline biomass and forming more glucose [37]. Also, using CO_2 as a pretreatment solvent causes low cost and no production of toxins. On the other hand, moderate operation conditions and high solid capacity make CO_2 explosion attractive. However, the excess equipment cost for safety cautions is an important barrier to large scale applications [178].

2.8.2.5 Liquid hot water

LHW or hot-compressed water is almost identical to steam explosion pretreatment. In LHW liquid water form at milder temperature (160°C-240°C) is used while steam is used in steam explosion [178]. The length of pretreatment time is varied from several minutes to hours [204]. The results of LHW pretreatment shows that it removes lignin, renders cellulose in the lignocellulosic biomass more reachable, avoids the generation of inhibitory compounds [205]. During LHW pretreatment, both hemicellulose and lignin solubilize in water and by this, hot water performing as an acid catalsyt, catalyze the reaction, displacement of oligosaccharides, hydrolyze polymeric sugars to form monomeric sugars, and they can be decomposed to aldehydes such as furfural from pentoses, acetic acid, HMF from xylose and formic acid [206-209]. Also, LHW pretreatment does not demand any chemicals or catalysts, requires moderate temperature, minimize degradation products, does not require any washing or neutralization step. Biomass size does not important because biomass particles are exploded during pretreatment [210-212]. However, high energy consumption cost due to the higher pressure and a large water consumption are the disadvantages of LHW pretreatment [182].

2.8.2.6 Microwave irradiation

Another physicochemical pretreatment method is the microwave irradiation (MWI) method. Electromagnetic field increases the temperature of the lignocellulosic biomass directly and thus, prevents to being temperature gradients. When comparing to conventional conductive methods, microwaves penetrate aqueous solution [213, 214]. Studies show that the lignin yield at MWI was greater than oil bath heating [181]. MWI treatment conditions are determined as 10 min at 250 W in 3% NaOH solution (w/v), and results show that the highest sugar yield and thus a combination of MWI and basic pretreatment method has a great potential to improve enzymatic process such as hydrolysis [215]. The combination of microwave pretreatment and other pretreatreatments such as chemical pretreatments have some advantages as enhancing lignin degradation; aqueous NaOH solution improves saponification of intermolecular bonds between hemicellulose and lignin [216]. Although MWI increases cellulosic degradation, porosity, hydrolysis rate of sugars and lignin removal, it requires high energy consumption and causes high cost. Thus, the commercial-scale application is difficult [181].

2.8.3 Biological pretreatments

The attraction for biological pretreatment is great because of its higher potential benefits than other chemical and physicochemical pretreatments. These benefits are specificity of substrate and reaction, reduction of energy consumption, no production of toxic compounds and high yield of desired products [217, 218]. Enzymes or microorganisms are applied to lignocellulosic biomass on biological pretreatment. Table 2.8 shows the activity of some microorganisms, their culture conditions, and degradation ratios.

Table 2.8 : Culture conditions and degradation ratios of some microorganisms.

Microorganisms	pH	Temp. (°C)	Time (days)	Degradation (%)	Reference
Cellulolytic and Hemicellulolytic Microorganisms					
Clostridium thermocellum	6.1-7.8	60	4-5	85-100	[219]
Thermotoga maritima	6.0-7.5	95	-	-	[220]
Ruminococcus albus	6.7-7.1	37	0.5-2	30-70	[221]
Fibrobacter succinogenes	6.1-6.8	38	0.5-3	54-79	[221]
Actitotalea fermentans	6.5	30-55	28	60	[222]
Trichoderma reseii	4.8	28	7	100	[221]
Ligninolytic Microorganisms					
Pseudomonas spp.	5.3-7.8	30	7-60	20-52	[221]
Trametes versicolor	-	25	28	9-24	[221]
Acinetobacter spp.	-	30	21-28	29-52	[221]

As it is shown in Table 2.8, the activities of microorganisms group are divided as cellulolytic and hemicellulolytic microorganisms and ligninolytic microorganisms. The cellulolytic and hemicellulolytic microorganisms only affect cellulose and hemicellulose structure. Lignin structure does not influence these microorganism groups. On the other hand, ligninolytic microorganisms are affected only lignin structure. For producing targeted products in the shortest time, multiple enzymes or microorganisms mixtures can be used on biological pretreatment [1]. Biological pretreatment method is trustable and environmentally friendly pretreatment method to increase lignin removal with less energy requirement [223]. However, hydrolysis rate after biological pretreatment is still at a low level and needs more researches [37].

2.8.4 Chemical pretreatments

Chemical pretreatment method is highly useful to increase the biodegradability of cellulose, separate lignin and hemicelluloses, reduce the rank of polymerization and break down crystalline form of cellulose in lignocellulosic biomass [224]. It is reported that some chemicals have a significant effect on lignocellulosic biomass structure, also do not generate toxic components and reaction temperature is at modarate temperature and pressure [225]. These chemicals are oxidizing agents, alkali, acid and salts, organic acids, mixture of organic solvent and inorganic acids [226, 227]. Ozonolysis, acid pretreatment, alkaline pretreatment, oxidative delignification, wet oxidation, ionic liquids, and organosolv process are the most common chemical pretreatment methods.

2.8.4.1 Ozonolysis

Ozonolysis is another chemical pretreatment method for lignocellulosic biomass. Ozone is required to break down of the structure of lignin and hemicellulose [228]. Also, cellulose was hardly affected [183]. Pasha and Rao indicate that, at ozonolysis pretreatment of poplar sawdust, enzymatic hydrolysis yield is improved up to 57% and lignin ratio is reduced from 29% to 8% [229]. According to another study which wheat and rye straw was ozonated at mild conditions, yields are increased up to 88.6% and 57% while these ratios are found as 29% and 16% in non-ozonated feedstocks [230]. As a result, in ozonolysis pretreatment, lignin is effectively removed, is not produced any toxic residues, reaction conditions are at mild temperature and pressure. Hence, this process is minimized environmental pollution [231, 232]. However, it requires a massive amount of ozone, and it causes high ozone cost [183].

2.8.4.2 Acid pretreatment

Acid pretreatment of lignocellulosic biomass is a traditional, well recognized, useful method and frequently used in present technology. Acid pretreatment parameters are acid types, the concentration of acid, temperature and solid to liquid loading rate [178]. At this process, the hydrolysis rate of hemicelluloses, a rate of amorphous cellulose, separate hemicelluloses that found in liquid fraction and cellulose that found in solid fraction are increased [41, 233, 234]. Acid pretreatment can be used lots of kinds of lignocellulosic biomass ranging from hardwood to grasses and agricultural residues [37]. In acid pretreatment concentrated and diluted acids used as a catalyst to break down crystallinity and rigid structure of lignocellulosic biomass. Especially H_2SO_4 and HCl are commonly used as concentrated acids for lignocellulosic biomass. Concentrated acids increase the yield of sugars at lower temperatures [1]. Although concentrated acids are strong agents for hydrolysis of lignocellulosic biomass, the application of these acids are not easy because of being corrosive, toxic, hazardous and requires extra safety equipment in reactors. Also, these acids must be recovered after hydrolysis for reducing acid cost [235].

Dilute acid is also used as lignocellulosic biomass. Different dilute acids such as H_2SO_4, HCl, H_3PO_4, and HNO_3 are used for acid pretreatment [184]. The concentration of acid is generally is 0.1-2% (w/v) at dilute acid pretreatment [178]. According to studies, in eucalyptus wood chips, the conversion of cellulose yield is achieved 80% and with an acid concentration of 1.84% in spruce wood chips obtained 40% cellulose conversion [236, 237].

The results of comparison for dilute acid and concentrated acid pretreatment, although dilute acid pretreatment consumes less acid and produces degradation product reduction than concentrated acid, it requires higher temperature and stronger conditions for obtaining high sugar yield [1, 195, 238]. The 2-stage sulfuric acid process is developed to overcome to drawbacks of acid pretreatments. At the first stage, 70% of the H_2SO_4 solution is used to hydrolyze hemicellulose and break the crystallinity of cellulose at 30-40°C. Then, acid is diluted with hot water to be 30-40%, and the temperature is increased 90-95°C. After the hydrolysis step, sulfuric acid is separated from other hydrolyzates by an ion exchange column. Then, recycling of sulfuric acid is required for using further acid hydrolysis [239].

Some organic acids such as maleic, succinic, oxalic, fumaric acids as dicarboxylic acid and acetic acid are used recently to avoid corrosion problems and requirement of less energy demand for acid recycling [1]. Maleic acid hydrolyzation yield is much as sulfuric acid but does not produce degraded products [240].

2.8.4.3 Alkaline pretreatment

Alkaline pretreatment is the application of base agents (NaOH, KOH, CaOH and NH_4OH) for pretreatment [182]. In alkaline pretreatment, the process mechanisms start saponification of intermolecular bond between xylan and other components [183]. One of the popular bases for alkaline pretreatment is NaOH. Lots of research were done about NaOH pretreatment until today and found that NaOH disrupts the structure of lignin and increases accessibility of enzymes to cellulose and hemicellulose [241, 242]. Also, it is found that pretreatment with sodium hydroxide is useful when the lignin ratio is lower than 26% [241]. Hence, alkaline pretreatment could be preferred for agricultural residues and herbaceous crops [69]. Pretreatment conditions are performed at ambient conditions, however, requires more pretreatment time at higher temperatures and because of removal of lignin and other inhibitory products, neutralization step is required before enzymatic hydrolysis [182].

Another alkaline method is using calcium hydroxide ($Ca(OH)_2$) which also known as lime, instead of NaOH. Lime could be applied for agricultural residues and hardwood residues [243, 244]. At lime pretreatment, the biomass particles which size of 10 mm or less pretreated with lime and water slurry and stored for a time of hours to weeks. Pretreatment time depends on temperature. High temperature reduce pretreatment time. Lime is used to separate lignin and hemicellulose and improves the crystallinity ratio [37]. Although the cost of lime is lower than sodium hydroxide, it involves calcium ions and calcium ions contact with oxalate and causes precipitation on plant equipment [69].

Ammonia is also commonly used in alkaline pretreatment for lignin removal. Pretreatment temperature is 170°C, ammonia concentration is 2.5-20% and the reaction time is 1 hour. Feedstocks are a mixture of corn and corn stover and switchgrass. At these conditions, delignification efficiency was found that 60-80% and 65-85% for mixture of corn and corn stover and switchgrass, respectively [245].

While comparing to other chemical pretreatment methods, alkaline pretreatment requires less temperature and pressure, and it causes lower sugar degradation than acid pretreatment. However, retention times vary from several hours to several weeks [246]. Although all drawbacks for alkaline pretreatment such as long reaction time, high energy demand and causing some sugar lost, alkaline pretreatment is ideal pretreatment method when both pentoses and hexoses are used as substrates for the fermentation steps [1].

2.8.4.4 Oxidative delignification

Oxidative delignification method is generally used for pulp bleaching, and commonly, ozone, oxygen, hydrogen peroxide, chlorine dioxide, sodium hypochloride, and chloride can be used as a catalyst [179]. In this process, the reaction occurs at mild conditions, and production of inhibitory compounds are strongly during oxidative delignification [183]. According to studies, lignin content of ozone pretreated wheat and rye straw was significantly reduced, but little hemicellulose degradation and loss of cellulose were occurred [230]. On the other hand, oxidative delignification cost is not competitive with conventional acid and alkali pretreatment methods; the application of oxidative delignification method is not commercialized as them [247].

2.8.4.5 Wet oxidation

Wet oxidation is treating lignocellulosic biomass with oxygen or air which act as a catalyst at a temperature up to 120°C [248, 249]. This method can be used to fractionate cellulosic structure from lignin and hemicelluloses, it is suitable for low lignin biomass such as wheat straw [69][250]. In this method, lignin is degraded to CO_2, H_2O, and carboxylic acids (R–COOH) [251, 252]. After wet oxidation pretreatment, up to 70% of lignin removes in lignocellulosic biomass [182]. Lissens et al. used lignocellulosic biowastes in their study and process conditions are 185 to 220°C temperature and 0 to 12 bar pressure. The feedstock is treated for 15 min and obtained enhanced the methane yield by approximately 35 to 70% [253]. Although high lignin delignification, during the wet oxidation process, a higher amount of byproducts are formed than steam explosion and they inhibit the enzymatic hydrolysis [250]. The combination of wet oxidation method with alkali methods, toxic material production is reduced such as furaldehydes and phenol aldehydes [252, 254]. However, detoxification step is required after wet oxidation pretreatment.

2.8.4.6 Ionic liquids

During the last decade, ionic liquids (ILs) application as a solvent for pretreatment has the increasing potential [255]. Ionic liquids are new type of salts which are used as solvents which have melting point lower than 100°C and exists in liquid state at ambient temperature, has wide temperature variety, high polarities, strong thermal and chemical durability, high ionic conductivity, is inflammability and volatility [1, 69, 256, 257]. Because of having a low boiling point, 99% of ILs are recoverable in some operations [182]. Because of having a recyclability status, ILs method is also known as a green solvent pretreatment method [1, 182]. Using ILs for lignocellulosic biomass as a solvent dissolve cellulose or lignocellulosic biomass forming homogenous solutions [257]. In addition, the available surface area of pretreated biomass is getting increased after pretreatment and enzyme can reachs easily in biomass [258]. ILs pretreatment involves at ambient temperature (90°C-130°C) and pressure for varying amount of time (1-24 hours) [259, 260]. Before enzymatic hydrolysis, the pretreated sample should be washed with water several times for detoxification [182].

Different ILs such as N-methyl morpholine-N-oxide monohydrate, 1-n-butyl-3-methylimidazolium chloride, 3-methyl-N-butylpyridinium chloride and benzyl dimethyl tetradecyl ammonium chloride can effectively used in different types of lignocellulosic biomass [178]. Although being environmental friendly pretreatment method for lignocellulosic biomass, ILs are still expensive and requires recycling. ILs pretreatment method should be developed for industrial application [1, 179, 261].

2.8.4.7 Organosolv delignification

In organosolv pretreatment method, organic or aqueous solvent such as low boiling point alcohols (ethanol and methanol), high boiling point alcohols (glycols), ketones (acetone), and organic acids (formic and acetic acid) is used with an inorganic acid (H_2SO_4 and HCl) and organic acid (oxalic, acetylsalicylic and salicylic acid) catalyst to pretreat lignocellulosic biomass [262-264]. Ethanol is the most commonly solvent in the organosolv process because of having a low boiling point, easy to recover and low toxicity [179]. In this process, lignin can be solubilized in an organic solvent and then, recovered, precipitated and reused for different purposes such as chemical or fuel and renamed as organosolv lignin [69]. Operation temperature is 150-200°C, pretreatment time is 30-100 min, solvent concentration is 30-75% (w/w), a liquid to solid loading ratio is from 4:1 to 10:1 (w/w), pH is between 2-3.8, and different lignocellulosic biomass can be utilized [37, 178]. For an economically and environmentally feasible process, solvents should be recovered by distillation. Also, the removal of the solvent is required due to its inhibitory effects on enzymatic hydrolysis [183]. Although recycling is increasing operational cost, having a high quality of lignin as a value-added product and having a low environmental impact [265]. The price and potential hazards of the high amount of organic solvent is a barrier to the utilization of organic process at large scales [179].

2.8.5 Literature review of LCF biorefinery pretreatment methods

Aguilar et al. (2002) were applied acid catalyst in their study. Sugarcane bagasse was selected as feedstock. Pretreatment temperature was varied from 100^0C to 128^0C, pretreatment time was 0 minutes to 300 minutes, and the acid ratio was between 2% to 6%. H_2SO_4 was selected as acid. According to tried conditions, the optimum results were found as 24 min, 122^0C and 2% of H_2SO_4. At this condition, pretreatment yield was found as 21.6 g/L of xylose, 3 g/L of glucose, 0.5 g/L of furfural and 3.65 g/L of acetic acid [266].

Eucalyptus residue was pretreated with H_2SO_4 acid in the study published by Canettieri et al. (2007). Pretreatment conditions were set as 0.65% (w/w) of H_2SO_4 ratio, 157^0C of temperature and 20 min of retention time. In this study, the pretreatment yields were found as 1.65 g/L of glucose, 13.65 g/L of xylose, 1.55 g/L of arabinose, 31 g/L of acetic acid, 1.23 g/L of furfural and 0.2 g/L of HMF [267].

One another acid pretreatment study was done by Orozco et al. (2007). While cellulose and grass were selected as feedstock, H_3PO_4 was chosen as an acid catalyst. The acid ratio was varied from 1% to 10%; temperature range was 150 - 200^0C and retention time differed from 0 to 15 min. The optimum results were found as 6.7% of xylose (w/w), 2.5% of arabinose (w/w) and 6.1% of glucose (w/w) at 15 min, 170^0C and 2.5% of H_3PO_4 ratio [268].

Corn stover was pretreated with acid in the study published by Cao et al. (2009). H_2SO_4 were selected as acid and ratio were varied from 0% to 32% (w/w). Pretreatment temperature was differed from 60^0C to 90^0C and retention time was selected between 0 to 240 min. At tried conditions, optimum results were found as 30% of reducing sugars and 7% of glucose yield at 90^0C with 31.8% of H_2SO_4 in 100 min [269].

Saha and Cotta (2006) published a study about alkaline pretreatment of wheat straw. 2.15% of H_2O_2 (w/w) was used as a catalyst. The pH of the medium was set as 11.5. The reaction temperature and retention time were selected as 35^0C and 24 h, respectively. At these conditions, reaction yield was found as 8.6% of monomeric sugars (w/v) [270].

Another alkaline pretreatment study was done by Kim and Holtzapple (2005). $Ca(OH)_2$ was used to provide alkaline conditions. Corn stover was treated with 0.5 g of catalyst in 55^0C for 28 days. Also, enzyme loading was set as15 FPU/g cellulose.

At these conditions, glucose and xylose yield was determined as 93.2% and 79.5%, respectively [243].

One of the most related pretreatment methods, the steam explosion was tested by De Bari et al. (2007). Aspen chips were used as feedstock, and pretreatment temperature was set at 205^0C. Retention time was varied from 3 to 10 min. At these conditions, the best xylose yield was found as 10.3 g/100g dry chips at 3 min retention time [271].

Steam explosion pretreatment method was chosen by Ewanick et al. (2007) to treat lodgepole pine samples. In their experiment, SO_2 was used as a catalyst with a ratio of 4% (w/w) at 200^0C for 5 min. According to their results, overall ethanol yield was found as 77% [272].

One other steam explosion experiment was done by Sassner et al. (2008). Pretreatment temperature was varied from 180^0C to 210^0C; retention time was tested at 4, 8 to 12 min and acid catalyst ratio was 0.25% to 0.5% (w/w). H_2SO_4 was selected as the acid catalyst in steam explosion pretreatment. At this study, the best result was found as 55.6% of total glucose and xylose yield at the temperature of 200^0C, for 4 and 8 min with the catalsyt of 0.5% of H_2SO_4 [234].

Linde et al. (2008) were treated wheat straw at a steam explosion pretreatment. 0.2% of H_2SO_4 was applied in steam explosion pretreatment at 190^0C. Retention time was set as 10 min. At these conditions, glucose and xylose recovery yield were found as 102% and 96%, respectively [233].

Liquid hot water pretreatment experiments were done by Dien et al. (2006). Corn fiber samples were treated with liquid hot water when the temperature was 160^0C and retention time was 20 min. At these conditions, arabinose and xylose recovery yield were determined as 74% and 54%, respectively [273].

Bermuda grass was treated with liquid hot water in the study published by Brandon et al. (2008). Different temperatures (200 - 230^0C) at various pressure and retention time were applied. However, pressure and retention time were not explicitly described. According to results, ethanol yields were found as 11 g/L and 14.7 g/L ethanol at 200^0C and 230^0C, respectively [205].

Perez et al. (2007) pretreated wheat straw with liquid hot water. Two different pretreatment temperature such as 170^0C and 200^0C were tested for up to 40 min retention time. Solid concentrations were tested as 5% and 10% (w/v), and pretreatment pressure was set as 30.6 atm. For producing bioethanol, commercial cellulase was used as an enzyme. At these conditions, sugar recovery yield was found as 53%, and the yield of enzymatic hydrolysis was calculated as 96% [274].

AFEX pretreatment was tried by Teymouri et al. (2004). Corn stover was selected as feedstock. Pretreatment conditions were temperature as 90^0C, ammonia to corn stover mass ratio as 1:1, moisture content as 60% and retention time as 5 min. According to results, glucose yield was determined as 98% and theoretically, ethanol yield was improved 220% of untreated corn stover samples [196].

One other AFEX pretreatment was applied by Murnen et al. (2007). Pretreatment temperature was 160^0C, ammonia to solid (biomass) ratio was set as 2:1 (w/w), moisture content was 233% and the retention time was 5 min. These experimental results were explained that 95% of glucan yield and 81% of xylan yield at 168 h of enzymatic hydrolysis [275].

Park et al. (2001) tried CO_2 explosion pretreatment to improve glucose yield on cellulose. The supercritical fluid was applied to the hydrolysis of cellulose and pretreatment conditions were determined as 160 atm of pressure, 90 min of retention time and 50^0C of temperature. Applied condition gave 100% of glucose yield at supercritical conditions [276].

1-butyl-3-methylimidazolium chloride, was selected as ionic liquid pretreatment. Ionic liquid pretreated wheat straw and steam exploded wheat straw selected as feedstock in the study which was published by Liying and Hongzhang (2006). Water was also used as a control in the ionic liquid pretreatment. The ionic liquid pretreatment results were indicated that the hydrolysis rate of wheat straw was found as 70.37% and hydrolysis rate of steam-exploded wheat straw was found as 100%. The water ratio at these conditions was determined as 42.78%, and 68.78% for ILs sample and steam exploded sample, respectively [277].

Another ILs pretreatment was done by Lee et al. (2009). 1-ethyl-3-methyl-imidazolium diethyl phosphate was selected as an ionic liquid at 30^0C for 30 min. *S. cerevisiae* was used to fermentation and yields were found as 54.8% of sugar reduction for 12 h enzymatic hydrolysis. Ethanol production per glucose was found as 0.43 after 26 h fermentation [278].

García-Cubero et al. (2009) tried ozonolysis pretreatment on wheat and rye straw. Room conditions were selected as pretreatment parameters in the ozonolysis pretreatment. While nonionated wheat and rye straw yields were 29% and 16%, yields were increased to 88.6% and 57% after ozonolysis pretreatment applied, respectively [230].

Wet oxidation pretreatment was selected in the study published by Varga et al. (2004). Corn stover was pretreated with alkaline and acidic oxidation. Pretreatment conditions were determined as 195^0C as temperature, 15 min as retention time and 12 bar oxygen pressure. Also, the cellulase enzyme was added into wet oxidation pretreatment when the temperature was 50^0C. The ethanol yield was found as 22%, 29%, and 83% when the enzyme loading was 73 FPU/g cellulose, 76 FPU/g cellulose, and 43.5 FPU/g cellulose, respectively [249].

2.9 Integrated Organosolv Based Biorefinery Overview

In the 3rd generation biorefineries, the main aim is the product more than one product at the same time. Besides, process integrations such as feedstock and product integration, heat integration, power integration, water integration, process synthesis, and LCA are integrated into the biorefinery. The integrated biorefinery which uses organosolv pretreatment is named as Integrated Organosolv Based Biorefinery (IOBB) from this point on. Thus, for a biorefinery approach, bioethanol, organosolv lignin, furfural, acetic acid, bioheat, and biopower were aimed to gain as products in the IOBB simulation. Process overview was shown in Figure 2.21.

In the IOBB, lignocellulosic based biomass, solvent, and catalyst are fed in the organosolv reactor. Two-phase (liquid and solid phase) occur during the reaction. Solid phase includes mainly cellulose and hemicellulose, sent to saccharification part for hydrolyzation and fermentation. Liquid phase includes a high quantity of solvent, water, solubilized lignin, solubilized hemicellulose, and a relatively small amount of furfural, acetic acid, and other solubilized components. The liquid phase is diluted with water for lignin precipitation and precipitated lignin separated from the liquid phase and the first product, organosolv lignin, is produced. The liquid phase is sent to the furfural production process. First of all, distillation requires for solvent recovery. Recovered solvent fed into organosolv reactor back. Next, the rest of liquor which

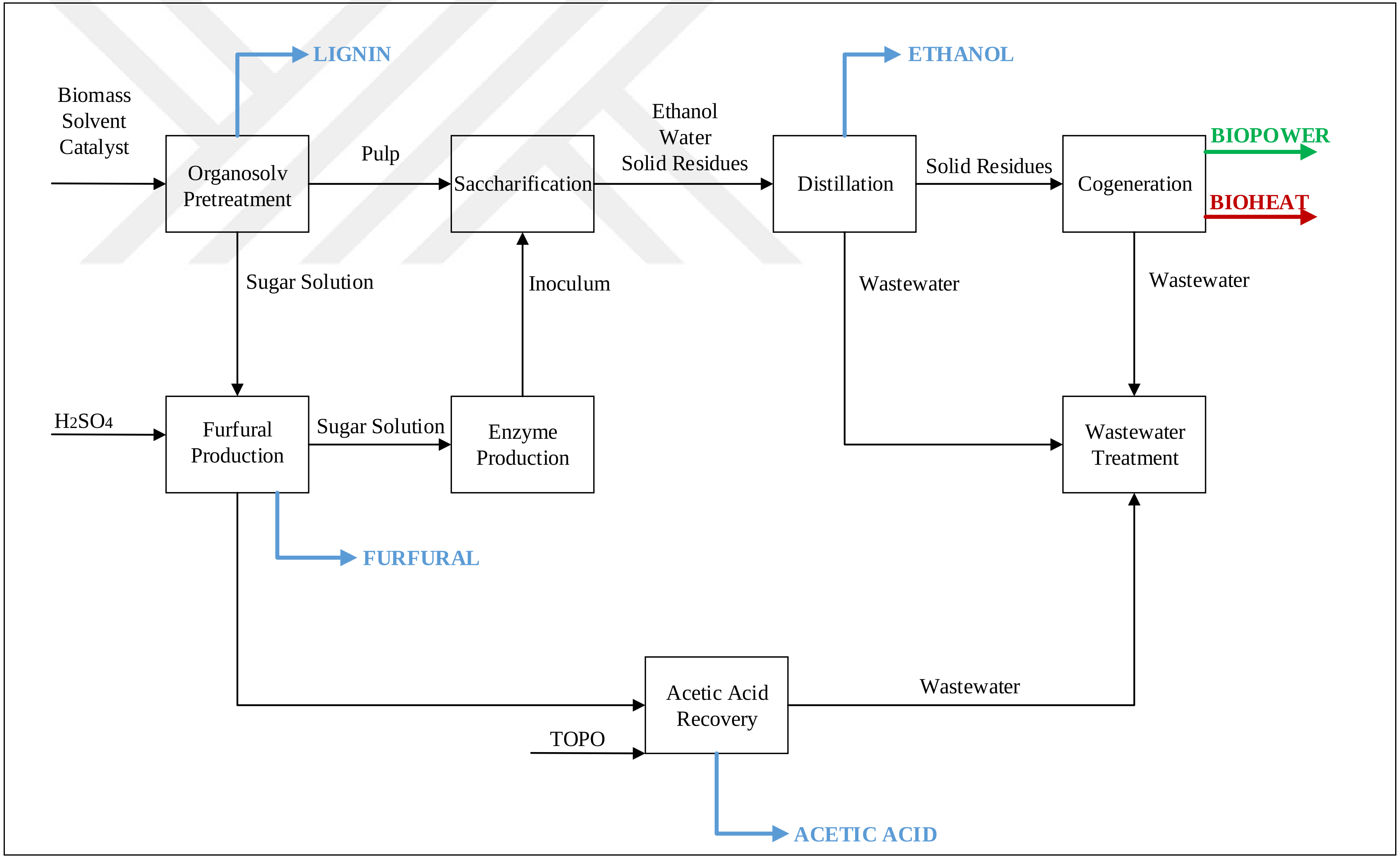


Figure 2.21 : Process overview for IOBB.

includes solubilized xylose is converted to furfural with the aid of H_2SO_4. Furfural is separated in the liquid phase with the aim of distillation. Hence, the other product, furfural, is produced. After distillation, two liquid phases are obtained. First one includes solubilized sugar components, and the other is the acetic acid rich solution. The sugar solution is sent to enzyme production, while acetic acid rich solution sent to acetic acid recovery step. For acetic acid recovery, liquid-liquid extraction is required. With the help of trioctyl phosphine oxide (TOPO), acetic acid is recovered from the solution as a third product. The rest solution is sent to wastewater treatment. Sugar solution which is obtained after furfural distillation is used for enzyme production. Inoculum is the nutrient-rich environment where the enzymes live in is generated from sugar solution and nutrients. Inoculum is sent to saccharification part. At saccharification part, the pulp is hydrolyzed and fermented with enzymes. Ethanol is produced in this step. However, it is required to distillate. In the distillation part, ethanol is separated from other components and obtained with high purity. Other streams in the distillation part are sugar-rich solution and wastewater. Sugar-rich solution is combusted in cogeneration part and produced biopower and bioheat, while wastewater is sent to wastewater treatment step. At wastewater treatment step, the content of wastewater is adapted to the legal limits. At last, all wastes and biogas from wastewater treatment are combusted, and bioheat and biopower are produced in the cogeneration process.

2.9.1 Organosolv lignin recovery

Lignin is one of the main bioproducts of the lignocellulosic biorefinery. Recovering lignin in biomass is great challenge for lignin production. Pretreatment methods are applied to hydrolyze biomass to separate cellulose, hemicellulose and lignin phase. Especially, organosolv pretreatment method is the best delignification method for lignocellulosic biomass. The major advantage of organosolv pretreatment is to obtain nearly pure lignin. Therefore, organosolv pretreatment is selected for lignin recovery. Organosolv pretreatment occurs in the presence of solvents (low boiling point alcohols, high boiling point alcohols, ketones, acids) and catalyst and lignin are separate from biomass in liquid phase [43, 48, 77, 279-284].

Lignin in the liquid phase should be precipitate to obtain organosolv lignin in pure and solid form. Therefore, water is added for precipitation. Generally, 1:7 to 1:10 ratio of solvent:water is applicable for organosolv lignin precipitation. Next, precipitated lignin is separated by filtration. Solid phase includes precipitated lignin and should be dried. Generally, 75% of total organosolv lignin is recovered after organosolv pretreatment [285, 286].

2.9.2 Furfural production

Furfural is one of the dehydration product of C5 sugars in lignocellulosic biomass. Synthetic production of furfural does not exist. In lignocellulosic biorefineries, furfural is produced by degrading of xylose in the presence of an acid catalyst or simultaneously xylose dehydration. In current biorefineries, simultaneously xylose dehydration is used for furfural production. However, furfural yield is low and unconverted C5 sugars are existed and discharge in wastewater. Using this unconverted C5 sugars in production, contribute the circular economy and reduce the environmental effects [287-291].

Furfural production process contains two steps such as furfural production and furfural purification/separation. The different acid catalyst can be used for furfural production. The most commonly used catalyst is H_2SO_4. Different studies indicate different furfural yield from xylose with a range of 50% to 80%. The application of H_2SO_4 catalyst requires 120-180°C temperature and 40 min to 1.2 hours retention time, solid to liquid ratio is 4:1 [50, 287, 292]. 0.48 M of H_2SO_4 catalyst application increased the furfural yield 90% [121-123, 129, 293-296].

Furfural and water form an azeotropic mixture in 35% by weight of furfural. While the furfural boiling is started at 161.7°C and 1 atm, it reduces 97.85°C in the mixture with water. To separate furfural-water mixture, azeotropic distillation, pressure swing distillation, adsorption, extraction, membrane separation, and molecular sieve method are applicable [293, 297-300]. Addition of solvents for breaking azeotropic mixture is available. These solvents are toluene, benzene, n–octyl acetate and n–butyl chloride [301].

2.9.3 Acetic acid recovery

Acetic acid production is occured from conversion of acetyl groups in lignocellulosic biomass, simultaneously. Acetic acid can inhibit the fermentation bacteria during the fermentation process at moderate concentrations. However, it is a valuable product in biochemical markets [302-304]. Recovering acetic acid from the liquid phase is time and energy consuming process in current technology [305]. However, it requires reducing wastewater toxic component content.

Liquid-liquid extraction, ultrafiltration, reverse osmosis, electrodialysis, distillation, liquid surfactant membrane extraction, anion exchange, precipitation, and adsorption can be applied acetic acid recovery in liquid fraction. Acetic acid cannot form azeotropes with water; however, a extensive equilibrium stages and increased reflux ratios are required for effective acetic acid recovery. Different entrainers can be added in distillation to reduce stage number and reflux ratio. In the precipitation method, calcium is added for acetic acid precipitation. However, waste quantity is very high in precipitation method [51].

Liquid-liquid extraction phase is separate acetic acid from liquid fraction and distillation separates acetic acid from extractants and undecane. Solvents of liquid-liquid extraction are ethyl acetate, trialkylamines, and trialkylphosphine oxide. Two different solvents are frequently used. These are TOPO and trioctylamine (TOA). TOPO ($[CH_3(CH_2)_7]_3PO$) is diluted in undecane ($C_{11}H_{24}$) and fed in the reactor with 1:1 (organic:aqueous phase volume ratio). TOPO is a strong solvating extractant, and strong hydrogen bonding acceptors induce the carboxylic acid to transfer to the extract phase. Also, high boiling point, strong chemical stability and reduced solubility in water are the main advantages of TOPO. However, because of the high cost of TOPO, undecane is required for dilution. Recycling reduces the cost of extractants. Additionally, TOA which diluted in octanol ($C_8H_{17}OH$) can be used as a solvating extractant, but recycling of TOA is difficult than TOPO [304, 306].

2.9.4 Bioethanol production

Bioethanol production includes pretreatment, enzyme production, saccharification, fermentation and distillation steps. Pretreatment steps which cause lignocellulosic biomass hydrolysis were described above. Saccharification converts polymeric sugars to monomeric sugars by hydrolysis. Hydrolysis could be acidic or enzymatic hydrolysis. Also, dilute, or concentrated acid is applied in acidic hydrolysis. Dilute acid is more commonly used process than concentrated acid hydrolysis. Dilute acid hydrolysis requires a higher temperature than concentrated acid hydrolysis but side reactions occur during dilute acid hydrolysis. Concentrated acid hydrolysis has high efficiency than dilute acid hydrolysis with less time [307]. The other type of hydrolysis is enzymatic hydrolysis. Generally, enzymes which named as cellulase are used to fastener saccharification step. Bacterias or fungus produce enzymes. Most common bacterias are *Clostridium, Cellulomonas, Bacillus, Thermomonospora, Ruminococcus, Bacteroides, Erwinia, Microbispora,* and *Streptomyces* while most common fungi are *Sclerotium rolfsii, P. Chrysosporium, Trichoderma, Aspergillus, Schizophyllum* and *Penicillium*. On the other hand, some mutant species such as *T. viride, T. Reesei,* and *T. Longibrachiatum* have a significant effect on cellulose destruction [183, 308].

Fermentation step converts monomeric sugars to ethanol in the presence of yeast. In current technology, the most used organisms for bioethanol fermentation are *Saccharomyces cerevisiae* and *Zymomonas mobilis* [309]. Theoretically, every kg of glucose and xylose convert 0.49 kg of CO_2 and 0.51 kg of C_2H_5OH [310]. Most of the mesophilic bacterias are used, and the required temperature is 30-34^{o}C. The optimum pH level is 6.5-7.5 for bacterias and 3.5-5.0 for fungus. The fungus is resistant to acidic conditions [311, 312].

Bioethanol forms azeotropes in water solution. Therefore, azeotropic distillation, pressure swing distillation or molecular sieve are required for bioethanol dehydration and purification. At azeotropic distillation, the third solvent is applied as an entrainer such as cyclohexane, benzene, acetone, diethyl ether, hexane, n-pentane and polymers [313-317]. The first step of azeotropic distillation is a beer column while 37% of bioethanol occurs. Then, the rectification column improves bioethanol purity to 95%. The last column is required to obtain high purity ethanol, nearly 99.6%. Therefore, bioethanol lost is reduced the minimum range [309, 310, 318, 319].

2.9.5 Wastewater treatment

All industrial production plants release wastewater during the production process. Also, biorefineries produce wastewater which contains degraded sugars and chemicals. The aim of wastewater treatment is reducing toxic materials in wastewater. Generally, the wastewater treatment process is proposed that anaerobic treatment, aerobic treatment, sludge removal/precipitation. Different processes are applicable such as reverse osmosis for salt removal, membrane filtration for total suspended solids and colloidal organic material removal, activated sludge system for organic load reduction and ammoniacal nitrogen removal, evaporation for volume reduction of reverse osmosis reject flow and crystallizer size reduction, crystallization for volume reduction of evaporator discharge and centrifugation for biological sludge dewatering [320].

For designing a wastewater treatment plant, first of all, chemical oxygen demand (COD) is calculated. Then, anaerobic digestion is applied to wastewater treatment. Anaerobic digestion general reaction is shown below [321].

$$\mathrm{C_vH_wO_xN_yS_z} + \left(\mathrm{v} - \frac{\mathrm{w}}{4} - \frac{\mathrm{x}}{2} + \frac{3\mathrm{y}}{4} + \frac{\mathrm{z}}{2}\right) \mathrm{H_2O} \rightarrow \left(\frac{\mathrm{v}}{2} - \frac{\mathrm{w}}{8} - \frac{\mathrm{x}}{4} + \frac{3\mathrm{y}}{8} + \frac{\mathrm{z}}{4}\right) \mathrm{CH_4} + \left(\frac{\mathrm{v}}{2} - \frac{\mathrm{w}}{8} - \frac{\mathrm{x}}{4} + \frac{3\mathrm{y}}{8} + \frac{\mathrm{z}}{4}\right) \mathrm{CO_2} + \mathrm{yNH_3} + \mathrm{H_2S} \tag{2.3}$$

Anaerobic digestion contains three steps such as hydrolysis, acidogenesis, and methanogenesis. pH is an essential parameter for anaerobic digestion. Decreasing pH also reduces the kinetic rate of anaerobic digestion. The optimum pH is accepted as 6.8-7.8. One other important parameter is temperature. Mostly, mesophilic bacteria is used and its optimum operation conditions at 30-38°C. Next, thermophilic bacteria can be used in anaerobic digestion at 50-57°C. Anaerobic digestion handles great COD quantities such as 3.2-32 kgCOD/m^3. Nutrient addition during anaerobic digestion is COD:N:P is set as 300:5:1. During anaerobic digestion microbial cell is formed ($C_5H_7NO_2$) and methane is released with 50-75% of yield. The rest occurs CO_2. The theoretical CH_4 yield is accepted as 0.4 L CH_4/g COD. Anaerobic digestion reduces nearly 90-95% of COD. Anaerobic digestion required less energy, less nutrient, smaller reactor volume, cause lower carbon print and the most important one is methane production which uses as an alternative energy source [321-324].

Aerobic digestion follows anaerobic digestion. The advantages of aerobic digestion are a requirement of shorter startup time, high removal of nitrogen and phosphorus, the requirement of low capital cost for small scale applications, no explosion risks and produce the biologically stable end product. Aerobic digestion handles smaller quantities of COD as 0.5-3.2 kgCOD/m^3. Aerobic digestion general reaction is shown below [321].

$$\mathrm{C_vH_wO_xN_yS_z} + \left(\mathrm{v} + \frac{\mathrm{w}}{4} - \frac{\mathrm{x}}{2} + \mathrm{y} + \mathrm{z}\right) \mathrm{H_2O} \rightarrow \mathrm{vCO_2} + \mathrm{yNO_2} + \frac{\mathrm{w}}{2} \mathrm{H_2O} + \mathrm{zSO_2} \tag{2.4}$$

CO_2, NO_2, H_2O, and SO_2 are released during aerobic digestion according to wastewater content. The temperature limits are between 20-40°C. Nutrient addition during aerobic digestion is 12.4% by weight of nitrogen [321].

After anaerobic and aerobic digestion, solid phase and liquid phase should be separate. Dewatering is a physical unit operation for separating water from sludge. Solid bowl centrifuge, belt filter press, recessed plate filter press, rotary press, screw press, electrodewatering, sludge drying beds, and sludge lagoons are some example dewatering processes [321].

After reducing pollutants in wastewater, the wastewater is discharging. The wastewater discharge limits are determined by governmental regulation and legislation. The wastewater should be in discharge standards before discharging. The discharge standards of petroleum refineries in Turkey is shown in Table 2.9.

Table 2.9 : Commercial wastewater discharge standards of the petroleum industry in Turkey (Refineries etc.) [325].

Parameter	**Unit**	**Composit sample (2h)**	**Composit sample (24h)**
Suspended Solid Material	mg/L	120	60
Oil and Grease	mg/L	20	10
Ammoniacal Nitrogen	mg/L	40	20
Hydrocarbons	mg/L	15	10
Sulfur (S^{-2})	mg/L	2	1
Phenols	mg/L	2	1
Crom ($Cr^{+6)}$	mg/L	0.2	0.1
Total Cyanide	mg/L	2	1
pH		6-9	6-9

2.9.6 Cogeneration

Cogeneration process is integrated into biorefineries to consume solid waste and methane, and convert it bioheat and biopower. Cogeneration process includes two steps which are combustion side and bioenergy (bioheat and biopower) production side. In current technology, fossil fuel is used in cogeneration for producing high energy valued gases. However, more pollutant gases occur. While lignocellulosic biomass contains low nitrogen and sulfur, the releasing of nitric oxide (NO_x) and sulfur dioxide (SO_2) gases reduces. Additionally, for being carbon neutral fuel, lignocellulosic biomass produces less net CO_2 emission to the environment [326].

At combustion side, a rich solid content phase combusted with air and produces heat and combustion gases such as hydrogen, carbon monoxide, carbon dioxide, methane, and other hydrocarbons. Theoretically, it operates 950°C with 99% efficiency. The excess air (10% - 50%) is fed into the combustion reactor to provide optimum conditions. Due to combustion, flue gases are released with very high temperature [327]. Solid waste which is ash and uncombusted solid occurs during combustion.

The second step is producing bioheat and biopower. The steam from the combustion reactor is fed into a steam turbine. Steam turbine converts hot and pressurized steam to mechanical energy. Mechanical energy drives a generator in a steam turbine, and biopower produces. Generally, the isentropic efficiency of the steam turbine is accepted as 0.8-0.9. The steam which is the outlet stream of steam turbine has low temperature and pressure, fed into a heat exchanger and bioheat is produced [328]. Government regulations determine the discharge limits of exhaust gas emission. Table 2.10 and Table 2.11 presents the air pollutants categories and discharge limits in Turkey [329].

Table 2.10 : Air pollutant categories [329].

Component	Classification	Category
Ethanol	Organic	3
Furfural	Organic	1
H_2SO_4	Inorganic	2
NO	Inorganic	4
NO_2	Inorganic	4
NH_3	Inorganic	4
Lactic Acid	Organic	2
Acetic Acid	Organic	2
Glycerol	Organic	3
Succinic Acid	Organic	2
SO_2	Inorganic	4
H_2S	Inorganic	2
Levulinic Acid	Organic	2
Formic Acid	Organic	2

Table 2.11 : Air pollutants discharge limits in Turkey [329].

Component	**Unit**	**Limit**
Inorganic component		
1.Category	mg/Nm^3	1
2.Category	mg/Nm^3	5
3.Category	mg/Nm^3	30
4.Category	mg/Nm^3	200
Organic component		
1.Category	mg/Nm^3	20
2.Category	mg/Nm^3	100
3.Category	mg/Nm^3	150

According to regulations of industrial air pollutant discharge limits, each category and their limits are determined. If more than one product exists in the same category, total emission is calculated for each category. For example, lactic acid and acetic acid are in the same category, and total lactic acid and acetic acid flowrates must be less than 100 mg/Nm^3.

2.9.7 Literature review of IOBB production

Manara et al. (2014) compared feedstock effects on organosolv pretreatment. In their study, comparison of olive kernels, grape pomace and seeds, and peach kernel were done. Formic acid and acetic acid mixture were selected as a solvent with the concentration of 30/50/20. The catalyst was not performed in their study. Solid to liquid ratio was set as 1:25, the temperature was 107°C and retention time was 180 minutes. According to their tried conditions, pulp yields were found as 75%, 64.4%, and 67.1%, organosolv lignin purity was obtained as 97.8%, 98.6% and 100%, respectively [330].

Feedstock size effects were studied by Baeza et al. (1991). 40 mesh sized and chip sized eucalyptus grandis were compared. 86% of formic acid with 0.22% of HCl catalyst were used in organosolv pretreatment. Solid to liquid ratio was set as 1:30, the reaction temperature was 90°C and retention time was defined as 90 minutes. At these conditions cellulose yield and delignification yield were found as 73.6% and 62.2% for smaller particles and 77.1% and 57% for chip-sized particles, respectively. It was concluded that smaller particles had higher delignification yield but slower cellulose yield [331].

Beechwood, Scots pine, and Norway spruce were compared by Hundt et al. (2013). 100% of glycerol organosolv pretreatment was applied for 8% of KOH catalyst for Beechwood and 10% of KOH catalyst for Scots pine and Norway spruce. 7% of solid ratio was applied for Beechwood, and 7.4% of solid ratio was applied for Scots pine and Norway spruce. The reaction temperature was 190°C for Beechwood and 210°C for Scots pine and Norway spruce. Retention time was set as 15 minutes for all feedstock type. At these applied conditions, cellulose yield was found as 81.5%, 80% and 80% for Beechwood, Scots pine, and Norway spruce, respectively. The results showed that the feedstock type had any significant effect on cellulose yield [332].

Solvent types were compared in the study which was published by Zhang et al. (2013). Sugarcane bagasse was used as feedstock, and 90% of glycerol, ethylene glycol and propylene glycol were compared. Constant pretreatment parameters were set as 1.2%

of H_2SO_4 catalyst concentrations, 1:10 of solid to liquid ratio, 130°C temperature and 30 minutes retention time. At these conditions, glucan recovery was found as 96.7%, 97.3%, and 96.8%, organosolv lignin recovery was found as 43.2%, 11% and 11% for glycerol, ethylene glycol, and propylene glycol, respectively. According to their results, while solvent types have no significant effects on glucan recovery, they have high impacts on organosolv lignin recovery. Organosolv lignin recovery of glycerol was higher than ethylene glycol and propylene glycol [333].

One other solvent comparison was made by Sidiras & Salapa (2015). They tried 50% of ethanol, methanol, diethylene glycol, acetone and butanol for pretreating 10 to 20 mm of wheat straw. 0.045 N of H_2SO_4 was added, solid to liquid ratio was set as 1:20, pretreatment temperature was selected as 160°C and retention time was defined as 20 minutes. At these conditions, delignification rates were found as 41%, 20.4%, 40%, 58% and 62.6% and cellulose removal rate was found as 8.5%, 13%, 12.2%, 12% and 13.4% for ethanol, methanol, diethylene glycol, acetone and butanol, respectively. At these results showed that delignification rate was effected from solvent type. However, cellulose removal rate was not effected from solvent type [334].

Gong et al. (2011) also compared solvent types such as ethanol and acetone. Solvent concentrations were 45%, no catalyst addition, 180°C temperature and 30 minutes retention time. Glucose recovery yields were 100% and 61%, organosolv lignin recovery yields were 64% and 61%, for ethanol and acetone, respectively. According to this study results, while solvent type was not a significant effect on organosolv lignin yield, they had important effects on glucose recovery yield. Therefore, this study indicated that using ethanol as a solvent have more bioethanol yield than acetone [335].

One other solvent comparison study was done by Nie et al. (2013). 60% of methanol, ethanol, n-propanol, and n-butanol were compared at the same conditions. 0.8 mm sized rice straw was used as feedstock and catalyst was not used. Solid to liquid ratio was set as 1:25, the temperature was selected as 75°C and retention time was defined as 180 minutes. According to their conditions, glucose yields were found as 29.82%, 28.19%, 26.15% and 39.39% for methanol, ethanol, propanol, and butanol, respectively. These results were shown that glucose conversion was not high at these conditions [336].

Sun et al. (2008), compared three types of glycerol for organosolv pretreatment. Tried glycerols were industrial crude glycerol, crude glycerol from sebacic acid production and crude glycerol from biodiesel production. In their study, the solvent concentration was set as 70%; catalyst was not applied, solid to liquid ratio was 1:20, the reaction temperature was 220°C and retention time was defined as 180 minutes and atmospheric pressure was applied. At these conditions, cellulose yield was found as 98%, 96%, and 95%, and organosolv lignin yield was found as 35%, 75%, and 85%, respectively. These results showed that, while cellulose yield was not effected glycerol type, organosolv lignin yield was affected by glycerol type. Crude glycerol from biodiesel production had better results than other types of glycerol. Additionally, glycerol organosolv pretreatment requires a higher temperature than other solvents such as ethanol, methanol, organic acids and ketones [337].

The studies which were published by Sun et al. (2004) and Xu et al. (2006), solvent comparison of organosolv pretreatment were done with acetic acid, mixture of acetic acid and formic acid, methanol, and ethanol. 0.7 mm sized wheat straw was used as feedstock. Constant pretreatment parameters were 0.1% of HCl catalyst usage, 1:20 solid to liquid ratio, 85°C temperature, and atmospheric pressure. Solvent ratios were set as 65%, 80% and 90% for acetic acid, 20/60/20 and 30/60/10 ratios for acetic acid/formic acid/water, 60% for methanol and 60% for ethanol. According to their study, the delignification results were found as 64.3%, 54.8%, 50.4%, 51.1%, 47.2%, 84.2% and 82.2%, respectively. Organosolv lignin removal was calculated as 78.2%, 80%, 88.2%, 89.4%, 94.1%, 23.5% and 37.4%, respectively. According to their studies, delignification rates are higher at low boiling point alcohols, and then, organosolv lignin removal is higher at organic acid solvents [338, 339].

Chen et al. (2015) compared solvent types, solvent concentrations, catalyst concentrations and retention time in their study. First of all, formic acid was selected. Solvent concentrations were 68%, 78% and 88%, H_2SO_4 catalyst concentrations were 0%, 0.05% and 0.1%, solid to liquid ratio was 1:10 and pretreatment temperature was 107°C. Retention time was 30, 60 and 90 minutes. According to their study, the best results for formic acid was obtained at 78% solvent concentration, without catalyst and 60 minutes retention time. At these conditions, the delignification rate was found as 75.2%, and glucose conversion was found as 50.1%. For acetic acid solvent usage, solvent concentrations were 70%, 80% and 90%, H_2SO_4 concentrations were between

0.1 to 0.3, solid to liquid ratio was 1:10 and pretreatment temperature was 110°C. Retention time was 60, 120 and 180 minutes were compared. The best results were found at 90% of solvent concentration, 0.3% of catalyst addition, and 120 minutes retention time. Delignification rate was found as 72.2%, and enzymatic glucose conversion was found as 21.3%. Also, catalyst concentration was compared in their study. 2 cm sized wheat straw was used with ethanol solvent with concentrations of 60% and 65%, H_2SO_4 catalyst concentrations were 30 mM and no catalyst. Pretreatment temperatures were 190°C and 220°C and retention times were 60 and 20 minutes. Delignification rates are found as 57.8% and 46.4%, respectively [281].

Cybulska et al. (2017) compared solvent concentration, catalyst concentration and temperature in their study. 1 mm sized date palm fonds were used as feedstock. Ethanol concentrations were 60% and 80%, and H_2SO_4 catalyst concentrations were 0% and 1.5%. Solid to liquid ratio was 1:10 and the retention time was 60 minutes. Pretreatment temperature was selected as 140°C and 200°C. According to their results, the best results were found at 200°C, non-catalyzed and 80% of solvent concentration with 43.05% of organosolv lignin removal and the worst results were found at 140°C, non-catalyzed and 80% of solvent concentration with 13.13% of organosolv lignin removal [45].

Erdocia et al. (2014) compared various solvents in organosolv pretreatment. Olive tree pruning chips were pretreated with 80% of formic acid, 90% of acetic acid and 30/60/10 ratio of formic acid/acetic acid/water ratio with 0.2% of HCl catalyst usage, 1:10 solid to liquid ratio, 130°C and 90 minutes. Organosolv lignin recovery rates were found as 79.01%, 69.05% and 69.09% for formic acid, acetic acid and formic acid-acetic acid mixture, respectively. It was seen in the results that, the organosolv lignin recovery rate was highest at the formic acid application and lowest at acetic acid application. However, results had no significant difference between results [340].

Acetic acid and formic acid used as solvents were compared by Zhao et al. (2010). Acetic acid and formic acid concentrations were applied as 93% and 88%, respectively. 0.1% of HCl catalyst was applied in acetic acid pretreatment, but no catalyst was used in formic acid organosolv pretreatment. Solid to liquid ratio was 1:10, the reaction temperature was 107°C for acetic acid and boiling point for formic acid, and the retention time was 180 minutes for acetic acid and 90 minutes for formic acid organosolv pretreatment. At these conditions, glucose and organosolv lignin recovery yields were found as 50.49% and 90.71% for acetic acid, 71.84% and 87.46% for formic acid organosolv pretreatment, respectively. These results presented that while organosolv lignin recovery was high at acetic acid organosolv pretreatment, glucose recovery yield are lower than formic acid organosolv pretreatment [341].

A study about catalyst comparison was done by Li et al. (2012). 20-40 mesh sized bamboo was used as feedstock in organosolv pretreatment. 88% of formic acid used as a solvent. Solid to liquid ratio was 1:20, the temperature was 101°C and retention time was 120 minutes. Catalyst concentrations were 0%, 1% of HCl and 3% of H_2O_2. At these conditions, organosolv lignin purity was found as 91.9%, 91.9% and 94.4% for non-catalyzed, HCl and H_2O_2 usage. It was seen in the results that, catalyst type and concentrations have no significant effect on the results in this study [342].

Another catalyst comparison study was done by Nie et al. (2013). They tried acidic (0.01 M HCl) and basic (0.25 M NaOH) catalyst in organosolv pretreatment. 0.8 mm size rice straw was used as feedstock, and constant pretreatment parameters were set as 60% of ethanol concentration, 1:25 solid to liquid ratio, 75°C temperature and 180 minutes retention time. Hemicellulose yield was 7.4% and 55%, organosolv lignin yield was 1.6%, and 9.3% and glucose yield was 26.39% and 8.17%, respectively. These results indicated that while acidic catalyst had higher results for glucose yield, had lower results for hemicellulose and organosolv lignin yield. However, comparison for other studies, these yields are lower, and for effective organosolv pretreatment, different conditions could be tried [336].

Temperature effects on organosolv pretreatment were tested by Koo et al. (2011). 40 mesh sized L.Tulipifera was used as feedstock. Ethanol was selected as a solvent with 50% of concentration. 1% of NaOH was used as a catalyst. Solid to liquid ratio was set as 1:10. 140°C, 150°C, and 160°C of temperature were tested with 50 minutes of retention time. At these applied conditions, glucan recovery yields were found as 60%, 60% and 59.3% and enzymatic conversion rates were found as 65.6%, 65.6%, and 6.8%, respectively. From the unknown reasons, 160°C had lower enzymatic glucose conversion than other applied temperatures. 140°C and 150°C had similar results in their study [343].

Baeza et al. (1991) tried different solid to liquid ratio such as 1:10, 1:20 and 1:30. They used eucalyptus grandis as feedstock. 99% of formic acid used as a solvent, and 0.22% of HCl was used as a catalyst. The reaction temperature was 90°C and retention time was 95 minutes. At these conditions, cellulose yield was found as 84.8%, 87.7%, and 88.3%; pulp yield was 41.3%, 42.1%, and 42.8%, respectively. The quantity of rejects were found 0.5% for 1:30 and 0.1% for 1:10 and 1:20. These results showed that the ratio of solid:liquid had no vital impact on cellulose and pulp yield. However, reject quantity was higher at reduced solid:liquid ratio. On the other hand, low solid:liquid ratio (1:30) increases solvent consumption and recycling of solvent causes more energy requirement [331].

A comprehensive organosolv pretreatment study was published by de la Torre et al. (2013). Ethanol and acetone were tried with different solvent concentrations such as 50%, 65%, and 80%. The acidic catalyst, H_2SO_4, was tested with different concentrations such as 0.001 N, 0.0055 N and 0.01 N. Temperatures were defined as 150°C, 170°C and 190°C and retention time were selected as 30, 75 and 120 minutes. For ethanol organosolv pretreatment, best results were found at 183°C, 30 minutes, 77.3% of ethanol concentration and 0.001 N of catalyst concentration. Organosolv lignin yield was found at these conditions as 87.03%. For acetone organosolv pretreatment, best results were found at 169.8°C, 120 minutes, 65.75% of ethanol concentration and 0.006 N of catalyst concentration. Organosolv lignin yield was found at these conditions as 87.1%. If the acetone and ethanol solvents were compared, while ethanol organosolv pretreatment had lower retention time and catalyst consumption, it requires more temperature and more solvent. At the best conditions for ethanol and acetone organosolv pretreatment, they had similar organosolv lignin yield [344].

Quesada-Medina et al. (2010) compared different solvents with different pretreatment conditions. They used hydrolyzed almond shells with a size of 0.2 to 0.5 mm. 100%, 75%, 50% and 25% of acetone, ethanol and 1-4 dioxane were tested as solvents. The catalyst was not used in their experiments. Pretreatment temperature was selected as 150°C, 170°C, 190°C, 210°C, and 230°C and retention time was defined as 10, 25, 40 and 55 minutes. At these tried conditions, best results were found as 75% of solvent at 210°C with 40 minutes for acetone, ethanol and 1-4 dioxane. Delignification rates were found as 79%, 72.8% and 87.6%, respectively [345].

Formic acid and acetic acid organosolv pretreatment were tried by Ligero et al. (2008). Eucalyptus globulus which was smaller than 1 mm particle size was used as feedstock. For formic acid organosolv pretreatment 80%, 87.5% and 95% of solvent concentration with 0.1%, 0.2% and 0.3% of HCl were tested. Solid to liquid ratios were tested as 1:10, 1:20 and 1:30. The reaction temperature was not defined in their study and retention time was selected as 60, 120 and 180 minutes. According to tried conditions, 180 minutes retention time, 1:30 solid to liquid ratio, 95% of formic acid concentration gave better results than other conditions. Pulp yield was found as 51.7% for formic acid organosolv pretreatment. At acetic acid organosolv pretreatment, 60%, 75% and 90% of acetic acid concentrations were tested with 0.1%, 0.3% and 0.5% of HCl catalyst. Solid to liquid ratio was set as 1:10 and retention time was selected as 60, 120 and 180 minutes. At these conditions, the best results were found at 60 minutes retention time, 60% of acetic acid concentrations, 0.1% of catalyst usage. At these conditions, pulp yield was found as 86.7%. For comparing formic acid and acetic acid organosolv pretreatment, acetic acid organosolv pretreatment had higher pulp yield with less retention time, less solvent concentration and less solid to liquid ratio. It means that acetic acid organosolv pretreatment requires less energy consumption because of less retention time, less solvent consumption because of higher solid to liquid ratio and low solvent concentration [346].

Oliet et al. (2002) tried ethanol and methanol with different pretreatment conditions. Solvent concentrations were 38%, 50% and 62%, solid to liquid ratio was 1:7, the reaction temperature was 176°C, 185°C, and 194°C, retention time was 56, 80 and 104 minutes. At these tried conditions, 176°C, 56 minutes and 62% of solvent concentration gave better results for ethanol and methanol. Total yield was 77.4% and 74% for ethanol and methanol solvent, respectively [347].

2.10 Process Simulation and Aspen Plus Simulation Software

The main aim of chemical process simulation is presenting physical and chemical conversions of chemicals via mathematical modeling which calculates energy and mass balances, phase equilibrium and chemical kinetics [348]. Increasing attention of chemical process simulation, some commercial and academic process simulators were developed and used frequently in chemical engineering applications such as Aspen Plus [349], Aspen HYSYS [350], CADSIM Plus [351], CHEMCAD [352], Design II for Windows [353], DWSIM [354], HSC Sim [355], ITHACA [356], PROSIMPlus [357] and PRO II [358].

Process simulators use FORTRAN, C++, and Visual Basic for calculation and forecast the different behavior of processes, analyze the process simultaneously with different cases and conditions, optimize the conditions with practical solutions, predict whole life of the process. The application of process simulators includes making energy usage efficient way, reducing operating costs and waste stream emissions, improving the process yield and efficiency, increasing the controllability of process and teaching the process design [348].

Through this software, Aspen Plus simulation software was chosen for process simulator in this thesis. Aspen Plus in a simulation software which had been developed by AspenTech software company in the United States of America (USA). ASPEN is the abbreviation of **A**dvanced **S**ystem for **P**rocess **En**gineering, and it was renamed as Aspen Plus since the latest version [359]. The application of Aspen Plus simulation software involves bulk chemicals, specialty chemicals and engineering & construction [349].

The flowsheet based solving technology is used in Aspen Plus simulation software. A whole chemical process simulation begins with raw material and lasts with the final product. Production steps contain input and output streams (material, heat, and energy) and unit blocks such as reactors, columns, heat exchangers, etc. [359]. The general scheme of running Aspen Plus simulation software is shown in Figure 2.22.

For developing Aspen Plus flowsheet, some steps which described below have to be followed [359].

1. Identifying the components used in the chemical process in “Properties Environment”. These components could be chosen from Aspen Plus databank or identifying components manually according to their thermodynamic properties.
2. Identifying thermodynamic models which perform by pure components or mixtures in the chemical process. These thermodynamic models are integrated into Aspen Plus simulation software.

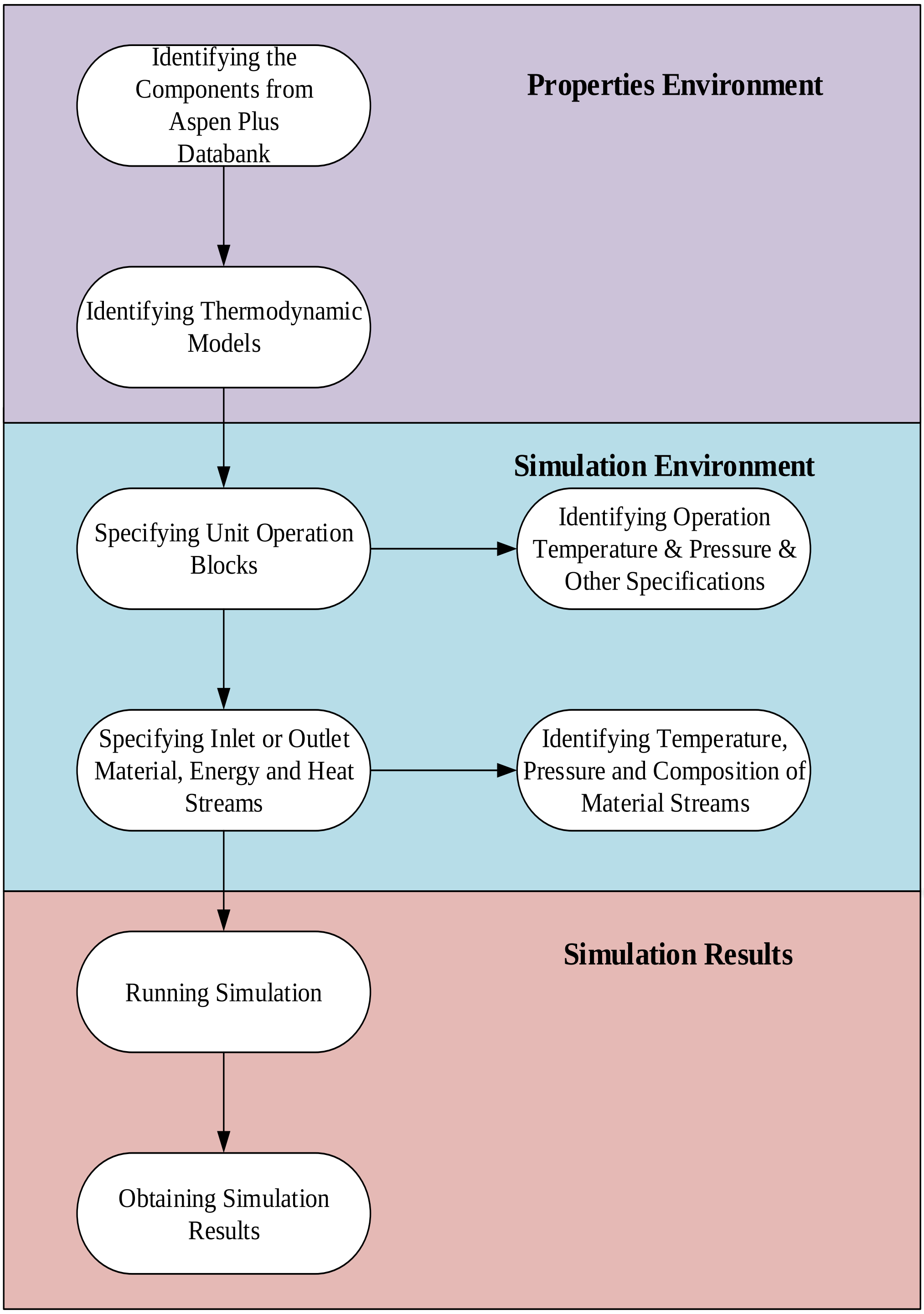


Figure 2.22 : General scheme of simulating Aspen Plus simulation software.

3. Identifying the process flowsheets in “Simulation Environment”:
    a. Specify the unit operation blocks.
    b. Specify the inlet and outlet material, energy and heat streams for unit operation blocks.
    c. Specify the thermodynamic models from Aspen Plus Model Library

4. Identifying flowrates and operating conditions such as temperature, pressure, and composition of all feed streams.
5. Identifying operating temperature and pressure for all unit operation blocks.

2.10.1 Templates

Aspen Plus simulation software contains built-in templates because of being user-friendly software. These templates are chemical processes, air separation, refinery, polymer, electrolytes, gas processing, metallurgy, pharmaceutical, polymers, and solid. Templates contain some information such as methods of physical properties, flow inputs (mass/molar/volume), stream report composition (mass flow/molar flow/volumetric flow), stream report format (generally mass basis) and stream class. On the other hand, blank simulation template can be used for process simulation. In the blank simulation, all properties environment data should be specified manually or selected from the database [360].

2.10.2 Units

Unit section exists in “Properties Environment”, and it is built-in or can be manually configurated for desired units. English engineering (ENG), metric engineering (MET) and international system (SI) units are available in Aspen Plus database. However, the user could be changed all or some of the units for its requests. While the flowsheet units are set in the unit selection section, different units can be used in individual unit operation blocks. Three different levels can be applied in the process. These are global unit set is for entire flowsheet, sheet unit is for individual form or an object and field unit is for an individual or a group of fields. This flexibility is a specialty of being user-friendly simulation software [360, 361].

2.10.3 Databanks

Aspen Plus system database includes several databases which contains physical parameters such as PURE10 (central pure component databank), ASPENPCD (Aspen Plus pure component databank), SOLIDS (solids databank), AQUEOUS (aqueous databank), BINARY (binary databank), COMBUST (combustion databank), INORGANI (inorganic databank), PURE 856 (pure component databank), PURE 93 (pure component databank), and AQU92 (aqueous databank). These databanks are available while the Aspen Plus is loaded. Other components could be added in the databanks [360, 362]. Help button gives detailed information about all databanks.

2.10.4 Components

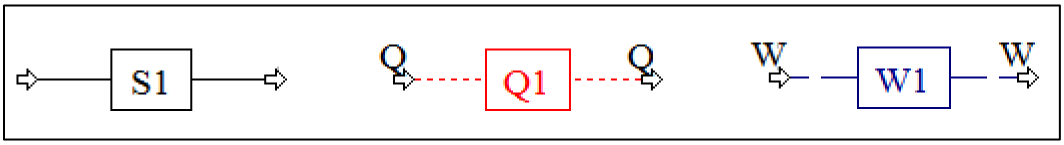
Components have defined the materials used in the chemical process. Aspen Plus Databanks includes a variety of materials and chemicals in any type such as solid, liquid and gases. Component identification (ID), type, component name, and alias are required in the component section. Component ID determines the name of the component which is given by the user. It can be variable if desired. Type contains, conventional, solid, nonconventional, pseudo component, assay, blend, hypothetical liquid, polymer, oligomer and segment selection. Suitable type should be selected. Component name is the name of the component which found in Aspen Plus Databanks, and it is unchangeable. Alias is the molecular formula. The components which are found in databanks can be easily added in component selection. However, the components which are not found in databanks should add in Aspen Plus component section. Thus, all thermodynamic properties and behaviors should be known for these components.

2.10.5 Physical Property Methods

Aspen Plus simulation software requires the data for thermodynamic calculations and transport properties. Thus, the sum of these models and methods create the physical property method. Thermodynamic properties are selected into fugacity coefficient, enthalpy, entropy, Gibbs free energy, and volume. Properties of transportation are viscosity, thermal conductivity, diffusion coefficient, and surface tension. The users can be used built-in and custom physical property methods. Ideal property methods, the equation of state property methods, activity coefficient property method and property method for unique systems are the main physical property methods which are available in Aspen Plus simulation software. Also, more than 20 sub-physical property methods are identified. The Ideal Gas, Raoult’s law, Henry’s law, Peng-Robinson, Redlich-Kwong, Redlich-Kwong-Soave, Hayden-O'Connell, non-random two-liquid (NRTL), UNIFAC, UNIQUAC, Van Laar and Wilson are the most frequently used methods for physical properties [360].

2.10.6 Streams

Streams provide connections between unit operation blocks and provide transportation of material, heat, and work are made via streams. These streams are shown in Figure 2.23.



(a) **(b)** **(c)**

Figure 2.23 : The display of (a) Material (b) Heat and (c) Work streams in Aspen Plus simulation software.

As it is seen in Figure 2.23, material streams are shown as a black line, and the names of the material streams start with “S”. Heat streams are shown as red dashes, and the names are starting with “Q”. Work streams are long blue dashes, and their names start with “W”. The streams can be defined as inlet streams into the flowsheet, interior stream in flowsheet, outlet streams from the flowsheet and pseudo-product stream which shows the flows in a block. In Aspen Plus simulation software, red indicators show the required streams while blue indicators show optional streams. Stream classes must be chosen according to the component and model type. Stream and substream classes are defined below.

2.10.6.1 Substream classes

Substream classes are chosen considered the component specifications. There are five substream definitions exist in Aspen Plus simulation software. The substream names and their specifications are described below.

- MIXED: for the fluid components
- CISOLID: for the conventional inert solids which present in the reactions however do not present in phase equilibria
- NC: for non-conventional solid components
- NCPSD: for non-conventional solid components with particle size distribution (PSD)
- CIPSD: Conventional inert solid components with PSD

PSD is the weight fractions of particle sizes, and the number of intervals and size of intervals can be defined by the user or by the program in Aspen Plus simulation software. Stream class is the combination of substream which can be used in the simulation.

2.10.6.2 Stream classes

In Aspen Plus simulation software, stream class choice is not obligatory if the solid components are not used in the simulation. However, the solid components often used. Thus, the stream class definition must be completed before the simulation is generated. The built-in stream classes are described below.

- CONVEN: The simulation does not contain any solid components, only MIXED
- MIXCISLD: The substreams are MIXED and CISOLID
- MIXNC: The substreams are MIXED and NC
- MIXCINC: The substreams are MIXED, CISOLID and NC
- MIXCIPSD: The substreams are MIXED and CISOLID with PSD
- MIXNCPSD: The substreams are MIXED and NC with PSD

The most convenient stream class is selected by user decision, and “Properties Environment” is completed. Then, for running simulation, some information is required. This information is input in the “Simulation Environment” section.

2.10.7 Unit operation blocks

The actual equipment is required for running the flowsheet of simulation. Minimum 1 unit operation block must be defined in the flowsheet before running. Selection of right equipment, fill all model and global block specification and specifying the work and heat necessity are fundamental properties of usage of unit operation blocks. In Aspen Plus simulation software, unit operation blocks classified as mixer/splitters, separators, exchangers, columns, reactors, pressure changers, solids, solid separators, and user-defined blocks.

2.10.7.1 Mixers/Splitters

Mixer and splitter blocks are used for combining and dividing the streams. Figure 2.24 shows the icons of the mixer and splitters.

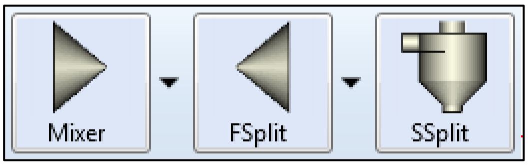


Figure 2.24 : The icons of mixer/splitters in Aspen Plus simulation software.

The first icon which shown in Figure 2.24 is a mixer. The mixer is known as stream mixer in Aspen Plus, and it is used for combining a variety number of material, heat or work streams. If heat or work mixers are applied in the flowsheet, the “Q” or “H” letters appear at the top-right of the icon. At least two inlets and one outlet streams are required for the running mixer. The outlet pressure and pressure drop could be specified in the mixer. Mixing tees and other mixing types of equipment can be modeled with mixers. The purpose of using FSplit is splitting the streams. At least one inlet and two outlet streams are required for FSplit. If FSplit has more than one inlet stream, firstly it combines the stream, then splits. If N number of outlet stream is available, (N-1) outlet specification must be specified based on molar, mass or volumetric flow. The composition and property of all outlet streams are identical. The only difference is the flow rates. FSplit is also used for heat and work streams. Flow splitters and purges or vents can be modeled with FSplit. The main difference between FSplit and SSplit is, SSplit splits substreams while FSplit splits main streams. It means that the user can arrange the outlet streams such as dividing liquid and solid phase into two streams. Solid stream splitters, bleed valves, purges or vents can be modeled with SSplit [360, 361].

2.10.7.2 Separators

Especially in chemical engineering, separators are one of the most used equipment in simulations. Separators are used for combining the inlet streams and split outlet streams based on the user has requested specifications or chemical behavior. In separators, temperature, pressure, heat duty and molar vapor fractions are available to input. For running separators, at least two output streams have to be specified. Separators split only material streams. However, heat and work inlet and outlet streams can be added to separators for supplying energy balances. Five different separators are used in Aspen Plus simulation software which shown in Figure 2.25.

Figure 2.25 : The icons of separators in Aspen Plus simulation software.

Flash2 is a flash distillation column with two outlet streams. Vapor-liquid or vapor-liquid-liquid phase equilibrium calculations can be performed in Flash2. One obligatory stream is vapor stream and is presented at the upper side of the icon. Other obligatory stream is a liquid phase and presented at the bottom of the icon. Also, optional water decant stream can be defined. Flash2 can be used as flashes, evaporators, single stage separators and knock-out drums in Aspen Plus simulation software. Flash3 is same as Flash2, except it has a vapor-liquid-liquid phase. The outlet streams consist of one vapor stream and two liquid streams. Flash3 can model any single stage separator. Decanter is designated for separating inlet streams, at the specific temperature or heat duty. Physical property method, distribution correlations which are formed by users, Fortran subroutines which are formed by users are used for calculating liquid-liquid distribution coefficients in decanters. The vapor fraction is not found in the decanter. If any vapor fraction exists, Flash3 is more convenient for modeling. Sep and Sep2 are modeled to split one or more streams which contents is known, but energy balances are not known or unimported. The main property of Sep and Sep2, the outlet streams can be specified as desired by users. Sep2 has wider specification variety such as component purity or recovery [360, 361].

2.10.7.3 Exchangers

Exchangers are the heat exchangers which change the thermal and phase conditions of streams. Heating and cooling curve tables can be generated for modeling heat exchangers. Heat exchanger models are shown in Figure 2.26.

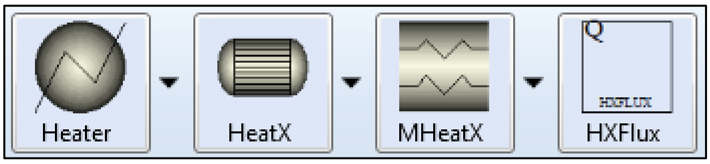


Figure 2.26 : The icons of heat exchangers in Aspen Plus simulation software.

The first icon in Figure 2.26 is a heater, and it is modeled as a heater or cooler. It has one inlet and one outlet material stream. Optionally, water decant stream can be added to the heater. Additionally, heat stream can be added as input or output stream. Temperature, temperature change, heat duty, vapor fraction, degrees of superheating and subcooling information can be defined in heaters. At least two of this information should be specified for running simulation. For modeling are one-side of heaters and coolers, valves which pressure drop is known and pumps and compressors which are not related to work. HeatX is used for two stream heat exchangers as a shortcut method or specific method. For running HeatX exchanger, the hot and cold inlet streams must be determined. Also, one of the other input of the hot or cold stream such as outlet temperature or temperature change, molar vapor fraction, degree of superheating/subcooling, heat exchanger duty, surface area for heat transfer, temperature approach have to be specified. MheatX is a multi-stream heat exchanger, and it performs heat transfer between a variable number of hot and cold streams. MheatX is not calculated heat transfer coefficient. However, it can calculate the overall UA. HXFluX provides heat transfer between a heat source and a heat sink via convective heat transfer. The function of log-mean temperature difference is used for calculation in HXFluX [360, 361].

2.10.7.4 Columns

Columns are identified as distillation columns. There are several distillation columns exist in Aspen Flus simulation software. Figure 2.27 shows the distillation columns.

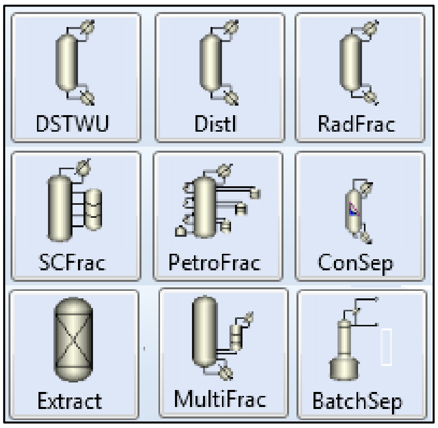


Figure 2.27 : The icons of columns in Aspen Plus simulation software.

DSTWU is a shortcut distillation column with a single input and two output stream with a partial or total condenser. Optionally, water decant stream can be added to the distillation column. DSTWU uses Winn-Underwood-Gilliland shortcut design for calculation. For running DSTWU, a number of stages or reflux ratio, light or heavy key component recovery ratio and condenser or reboiler pressure should be specified. DSTWU can produce a table or graph of reflux ratio versus stage. Distl is a shortcut distillation column which uses the Edmister approach for separating inlet stream into two outlet streams. Some theoretical stages, reflux ratio, and overhead product rate should be specified. SCFrac is a shortcut distillation column for petroleum. SCFrac can estimate product composition and flows, stages numbers and heating or cooling duty. Solid fractions are not suitable for SCFrac. RadFrac is available for 3-phase systems, narrow-boiling, and wide-boiling systems and nonideal robust liquid phases systems. RadFrac models systems such as absorption, stripping, extractive, and azeotropic distillation. MultiFrac is rigorous distillation column which consists of elaborate columns with any number of stages and connections. PetroFrac is same as MultiFrac but uses in petroleum units such as atmospheric crude unit, vacuum unit, etc. RateFrac is rate-based distillation model for non-equilibrium separation. The simulation represents the actual tray and packed columns. Two-phase systems, reactive and nonreactive systems, and electrolyte systems can be modeled with RateFrac. BatchSep is a rigorous batch distillation column and suitable for narrow- and wide-boiling, strong non-ideal, 3 phase, and reactive systems. Reactions are not available in BatchSep. The Extract column is used for liquid-liquid extraction. For configuration Extract column, thermal options and stage number should be specified. Principal components and the stage of the streams must be determined. Temperature and pressure estimation could be available in this equipment [360].

2.10.7.5 Reactors

In Aspen Plus simulation software different chemical reactors can be used for chemical reactions. According to known and unknown data, the appropriate reactor should be selected and used for calculating. Heat is not required at reactors. However, it can be added optionally. Figure 2.28 shows the icons of the reactors which used in Aspen Plus.

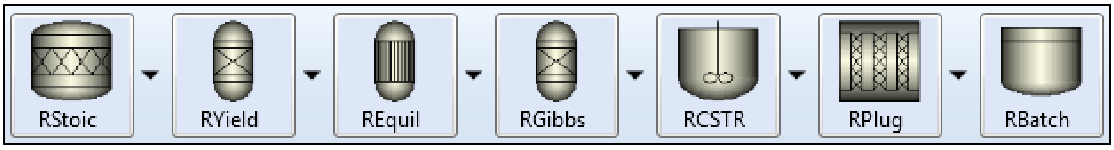


Figure 2.28 : The icons of reactors in Aspen Plus simulation software.

RStoic is a stoichiometric reactor, and it is used when the stoichiometry of the reaction is known. Temperature, pressure, vapor fraction, heat duty can be specified. At least two of them must be identified. Also, the reaction stoichiometry and molar extend or fractional conversion are required. Both series and parallel reactions are available for RStoic. If the stoichiometry and kinetics of a reaction are unidentified and yield of a reaction is known, RYield reactor is applied. Temperature, pressure, heat duty or vapor fraction and reaction yield should be specified in this type of reactor. If some reactions achieve equilibrium, REquil reactor model should be used. Single or simultaneous phase equilibrium and chemical equilibrium reactions are available for REquil. Approaching temperature and molar should be identified in REquil reactors. Also, RGibbs reactor is used for single or simultaneous phase equilibrium and chemical equilibrium reactions. Reaction stoichiometry is not required for RGibbs reactor. Temperature, pressure or heat duty is the primary inputs for RGibbs reactor. RCSTR is a continuous stirred tank reactor (CSTR) and uses when the reaction kinetics is known. The properties of the outlet stream of the CSTR reactor are the same as the content of the reactor. In contrast to RCSTR reactor, the composition of RPlug reactor varies along its length. The coolant temperature and overall heat transfer coefficient have to be determined or calculated by the subroutine. Additionally, the temperature of the cooler should be provided. Reactor dimensions such as length and diameter could be determined. RBatch block is used to design a batch reactor. In RBatch reactor, chemical equations are determined. The overall energy balance should be determined as the function of time [360].

2.10.7.6 Pressure changers

Different type of pressure changers is designed in Aspen Plus simulation software. These are a pump, compressor, multi-stage compressor, valve, pipe, and pipeline. The icons of pressure changers present in Figure 2.29.

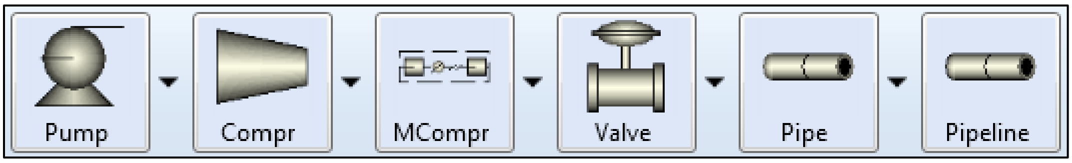


Figure 2.29 : The icons of pressure changers in Aspen Plus simulation software.

The pump is generally used to compute the power requirement of fluid up to specific pressure. This model is also used to design the hydraulic turbine. The discharge pressure, pressure increase, pressure ratio or power required should be defined in pump blocks. The Compr block is used to design a single stage compressor. Isentropic, polytropic and positive displacement models should be selected for the compressor. If the compressor wants to design with multiple stages, MCompr block should be selected. Stage number, compressor model (isentropic, polytropic and positive displacement), specification type (fix discharge pressure from the last stage, fix discharge conditions from each stage and use performance curves to determine discharge conditions), rating option (use performance curve to determine shaft speed) and heat capacity calculations are the selections of multi-stage compressor. Valve, pipe, and pipeline are stable blocks to involve resistance to flow that has to be overcome by the use of a pump or compressor [360].

2.10.7.7 Solids

Solids category which presents in Figure 2.30 includes nine different icons such as crystallizer, crusher, screen, single stage solid washer, counter-current decanter, dryer, granulator, classifier, and fluid bed.

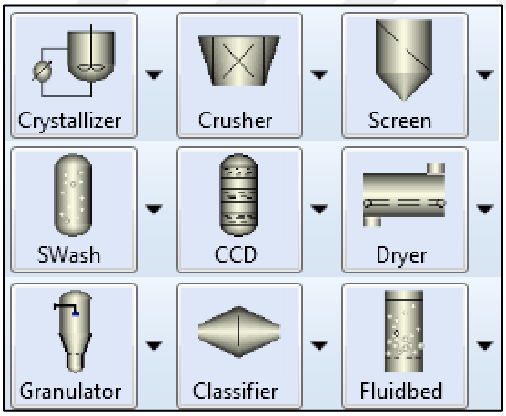


Figure 2.30 : The icons of solids in Aspen Plus simulation software.

Crystallizer is modeled for removing solid products in suspension. Mass and energy balance calculations can be used in the crystallizer. Additionally, size distribution can be applied for crystallizer. Two parameters such as temperature, heat duty, flow rate of product or vapor should be defined. One of the saturation calculation methods such as solubility data, solubility function, chemistry or user subroutine should be selected. One other selection is operating mode such as crystallizing, dissolving or melting. Gyratory jaw crushers, single-roll crushers, multiple-roll crushers, cage mill impact breakers are designed in crusher block. The aim of using a crusher block is reducing solid particle size. The heat releasing during crushing is not calculated in crushers. The screen is used for the solid separator according to particle size distribution. The desired particle size is obtained for designing screen. Solid particles from a liquid separate by SWash. Liquid to solid ratio and mixing efficiency are determined in SWash. Counter-current decanter or multistage washer are designed by CCD bock. Working pressure of equipment, mixing efficiency, stage number, and the liquid:solid ratio of each stage are calculated by counter-current decanter. The dryer is used to dehydration of solids. Shortcut, convective dryer, spray dryer, and contact dryer models are modeled by dryer icon. Pressure and heat duty, superheat, temperature or temperature change should be defined in dryer [360, 361].

2.10.7.8 Solid separators

Cyclone, venturi scrubber, centrifuge, rotary vacuum filter, centrifuge filter, hydrocyclone, fabric filter, and electrostatic precipitator are modelled with solid separators. Solid separators in Aspen Plus simulation software is shown in Figure 2.31.

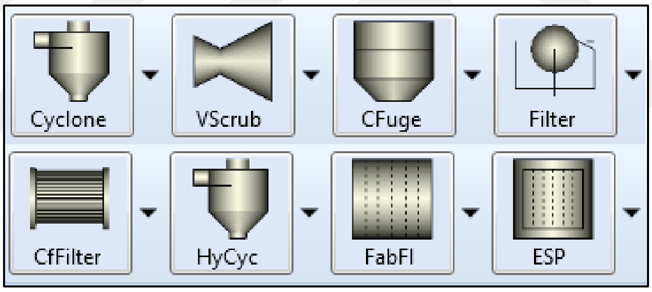


Figure 2.31 : The icons of solid separators in Aspen Plus simulation software.

The cyclone is used for cyclone separators. It removes solid components in a gas stream using the centrifugal force. Venturi scrubber (VScrub) separates solid particle in a gas stream by straight touch with an atomized liquid stream. Centrifuge (CFuge) separates liquids and solid particles with the centrifugal force. The efficiency of the rotary vacuum filter (Filter) is equal to 1, and the outlet stream does not contain any solid particle. CfFilter is also powered by centrifugal force to separate solid particles. Also, HyCyc, hydrocyclone separates solid particles in liquid streams by using centrifugal force. Fabric filter (FabFl) contains vertical fabric cells and separates solid particles in gas streams. An electrostatic precipitator (ESP) is used electrostatic force to remove solid particles in the gas stream [360].

2.10.8 User-defined blocks

User-defined blocks allow simulating user desired blocks with the aid of Fortran statements or excel spreadsheets. Hierarchy blocks and calculator blocks are examples of user-defined blocks.

2.10.8.1 Hierarchy blocks

Hierarchy blocks are used in complex simulation to provide the hierarchical design. Hierarchies can contain streams, blocks or other hierarchies. In complex simulations, different processes are designed in different hierarchies to make the simulation more readable and understandable. Additionally, essential parts of a process may be separate by hierarchy block. The material, work and heat streams between hierarchies are shown in the main flowsheet as input and output streams [360].

2.10.8.2 Calculator blocks

Calculator blocks are allowed to modify the stream contents according to the user requested. Calculator block usage is determining the flowsheet variables which the block samples or manipulates, submitting the formulas that used in Excel or Fortran statements and determining. Calculator blocks alter the stream specification. For example, a calculator block is defined in a stream and determined that this stream is 10% of another stream. While the second stream is changed, the calculator block automatically changes the first stream and set as 10% of the second stream. The usage of calculator blocks allows the user that applied a block in different runs without any input specification [360].

2.10.9 Literature review of process simulation and Aspen Plus simulation software

Weinwurm et al. (2016) compared both experimental and simulation studies about lignin concentration from ethanol organosolv liquors. Aspen Plus simulation software was used, and the Non-Random Two Liquids Redlich Kwong (NRTL-RK) property method was used for the thermodynamic calculation. While experimental study results presented that lignin rejection rate was 99%, process simulation gave the result as 90% [363].

Vila et al. (2003) compared the organosolv pulping experimental and simulation studies. Aspen Plus simulation software was selected for simulation. *Eucalyptus* *globulus* wood chips were used as feedstock, and organosolv pretreatment parameters were determined as 130^{0}C for 3 hours, 10 kg liquor/1 kg dry wood as a liquid to solid ratio, 0.2% of HCl and 90% acetic acid. Organosolv pretreatment, solvent, and catalyst recovery, lignin and furfural recovery, and secondary solvent recovery were the designed process that used in the simulation. According to calculations, acetic acid recovery was found as 97.6%, and HCl recovery was calculated as 91.7% [364].

Peralta-Ruíz et al. (2012) compared simulated case studies about bioethanol production process from residual microalgae biomass. Aspen Plus simulation software was used, and thermodynamic model NRTL (Non-Random Two Liquid) was selected as a model for simulation. The component selection was made with Aspen Plus database and NREL database of biofuel components. Three cases were compared, and these are CS-1, simultaneous saccharification, and co-fermentation (SSCF), CS-2, simultaneous saccharification and fermentation (SSF) and CS-3 separate saccharification and fermentation using acid hydrolysis (SHF). At the end of each case, molecular sieves were added for dehydration of bioethanol. Results of simulation show that in CS-1 bioethanol yield was found as 23.6%, being the highest of the routes determined, CS-2 and CS-3 present the yields of 20.1% and 18.5%, respectively [365].

Fasahati and Liu (2014) published an article about commercial scale bioethanol production that used brown algae as feedstock. They used Aspen Plus simulation software for modeling the biorefinery. Thermodynamic model, NRTL, was selected as a model for simulation and components were defined from Aspen Plus database. The missing components were completed according to the NREL database of biofuel components. Two pretreatment processes such as acid thermal hydrolysis and hot water wash pretreatment on bioethanol production were compared in economic terms. Lowest selling price of ethanol for hot water wash pretreatment and acid thermal hydrolysis were calculated as 0.63 $/L and 0.75 $/L for 80 kt/y scale and 0.55 $/L and 0.62 $/L for 400 kt/y scale, respectively. Therefore, acid thermal hydrolysis was found to be more efficient for bioethanol production [366].

The simulation of furfural production was published by Morales et al. (2010). H_2SO_4 was used for a catalyst for furfural production. Aspen Plus simulation software was applied for simulation. UNIF-LL method was selected for furfural distillation stage 1, and UNIFAC method was selected for furfural distillation stage 2. In column 1, the number of stages was set as 30, and feed stream was 3, condenser type was the total condenser, phases were vapor-liquid, reflux ratio (mass) was 5 and distillate to feed ratio was determined as 0.08. In column 2, the number of stages was selected as 24, condenser type was the total condenser, phases in column were vapor-liquid-liquid, convergence type was azeotropic distillation, reflux ratio (mass) was 9, distillate/feed ratio was 0.08, and the subcooled temperature was 50^0C. According to simulation results, 75 % of furfural production yield was achieved [50].

Rahimi et al. (2019) present the commercial biodiesel, biogas, and bioheat production. Castor and *Eruca sativa* plants were used as feedstock. Aspen Plus simulation software was selected for simulation. The physical parameters were selected as NREL model for the liquid phase, SRK model for gases phase, Henry's law components for CH_4, CO_2, O_2, and N_2 in the gases phase. Also, Aspen Plus database and NREL components for biofuel database were used to define the components used in the simulation. The case studies are defined as biodiesel production by transesterification of oil extracted from castor (CS-1 and CS-3) and *Eruca sativa* (CS-2 and CS-4) grains, biogas or heat production from lignocellulosic residuals (CS-3 and CS-4). The results of the simulation present that biodiesel production was 7400–7470 m^3 per year in these processes. The cost of biodiesel was found as 0.28 $/L for CS-1, 0.04 $/L for CS-2, 0.31 $/L for CS-3 and 0.02 $/L for CS-4. These results indicate that the most profitable scenario was CS-4, while the highest cost was required for CS-3 [367].

Sugarcane biorefineries with fossil fuel co-combustion to produce bioethanol, biomethanol and biolactic acid were simulated and compared in the study which was published by Mandegari et al. (2018). Bioethanol production contains pretreatment, enzyme production, SSCF, ethanol purification, molecular sieve, evaporation, wastewater treatment, and CHP unit. Biomethanol production includes drying, gasification, combustion, steam generation, a compression unit, rectisol unit, synthesis reactor, methanol purification, and CHP unit. Biolactic acid production occurs from the steps such as pretreatment, enzyme/strain production, SSCF, filtration, evaporation, decomposition, distillation, evaporation, water treatment, and CHP unit. Each production was divided into two scenarios in which self-energy-sufficient and non-self-energy-sufficient. The results were presented that for all scenarios which contain fossil fuel consumption (coal), improve the total capital cost 26–33%, however production sales increase in the range of 28–43% [368].

2.11 Life Cycle Assessment and SimaPro Software

This section presents detailed information about, firstly, environmental impact assessment methods of LCA and methodology of LCA. Next, LCA software, especially SimaPro software and databanks of software are presented. Lastly, a literature review about LCA is presented.

2.11.1 Environmental impact assessment methods and Life Cycle Assessment

Industrial and business developments and increasing consumption require more production, more raw material, and energy usage. Therefore, the societies had worried their impacts on natural resource depletion and environmental degradation [369]. Environmental impact assessment awareness was born directly proportional to increasing the societies consciousness. Accordingly, at the United Nations Conference on Environment and Development which was done in 3 – 14 June 1992 in Rio, published a declaration by the United Nations World Commission on Environment and Development (UN WCED) and it was mentioned that all countries, people and critical sector of societies had to work about integrity of developmental systems and global environment by international agreements [370]. One of the most approved methods for determining the effects of systems and products on the environment is LCA [371]. According to report which was published by Environmental Protection Agency (EPA), the term of “life cycle” contains the main activities such as manufacturing, using and its final disposal of a product during its life-span [369]. Figure 2.32 shows the stages of a life cycle.

The studies about LCA had begun in the 1960s. The cumulative energy requirements of chemicals and products had been calculated and published by Harold Smith at the World Energy Conferences in 1963 [369]. The years between 1970 to 1990 are known as “Decades of Conception”. Midwest Research Institute (MRI) was done the first study to calculate resource, emissions and waste quantities for Coca Cola Company in 1969. Unfortunately, it was not published. Then, similar studies were done by other

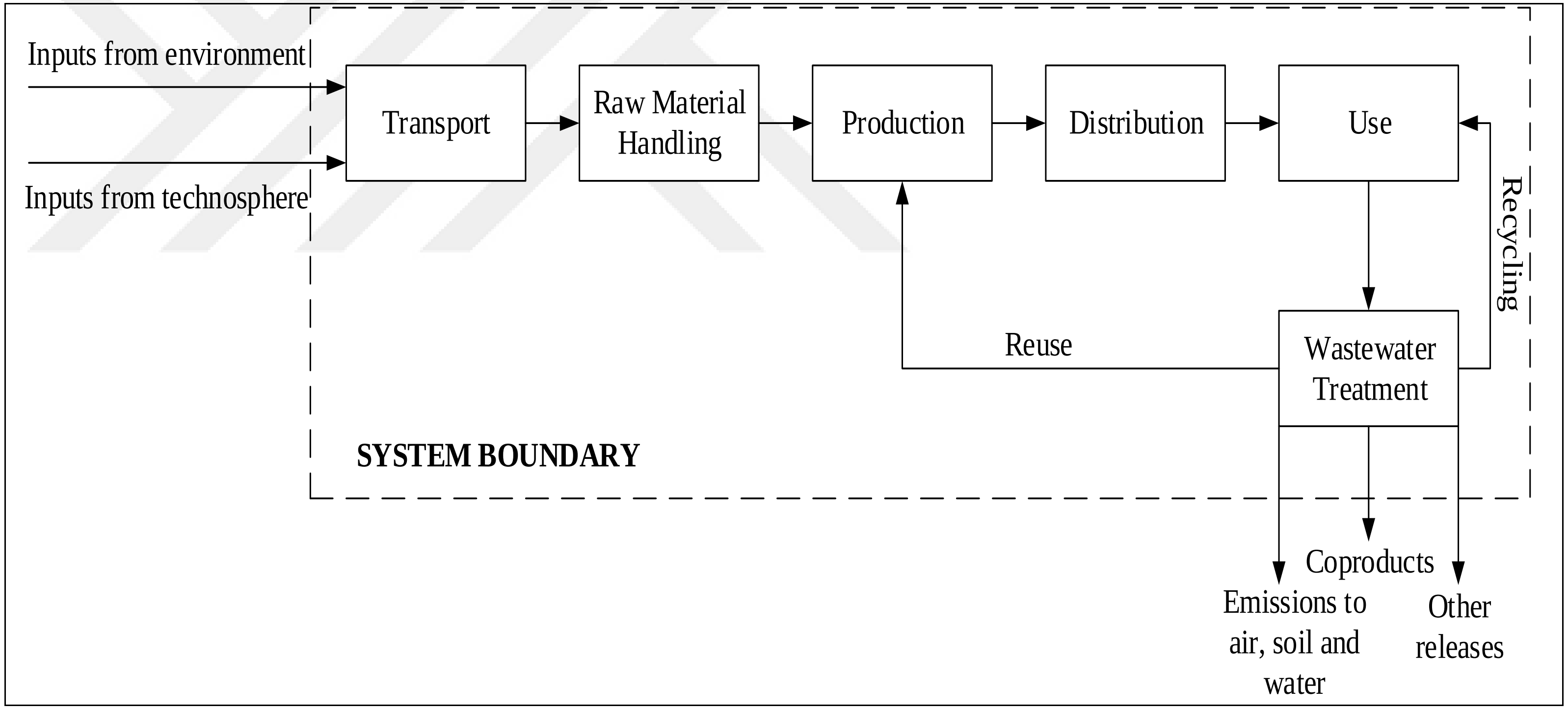


Figure 2.32 : The main LCA stages of a system, adapted from [55, 56, 372].

companies in Europe and the US [373]. In the US, the term of the process of evaluating the resource requirement and environmental effects of products is named as Resource and Environmental Profile Analysis (REPA). It was known as Ecobalance in Europe. In these years, different methods were used for LCA calculations. Thus, similar studies had greatly varied results, and it prevented globalization of LCA. Then, the years between 1990 to 2000 are known as "Decade of Standardization". In the 1990s, the numbers of scientific researches, common activities, guides, handbooks, and journal articles were greatly increased. The Society of Environmental Toxicology and Chemical (SETAC) lead and coordinated to LCA researchers and developed framework, terminology, and methodology of LCA. Afterward, the International Organization for Standardization (ISO) had been started to work about LCA in 1994. ISO published ISO 14040 series for standardization between 1997 to 2002 [369, 373, 374]. ISO 14040 series include:

- ISO 14040:1997, 2006: "Principles and framework"
- ISO 14041:1998: "Goal and scope definition and inventory analysis"
- ISO 14042:2000: "Life cycle impact assessment"
- ISO 14043:2000: "Life cycle interpretation"
- ISO 14044:2006: "Requirements and guidelines"

The years after the 2000s are known as "Decade of Elaboration". The United Nations Environment Programme (UNEP) and SETAC were associated as an International Life Cycle Partnership and was named as Life Cycle Initiative and aimed to develop the validating tools through advance data and indicators and converted life cycle thinking into practice. Communication on Integrated Product Policy (IPP) was defined as the importance of the LCA and its applications in 2003. Then, the European Platform on LCA (2005) to related LCA methods and data in business and policy [369, 373].

2.11.2 The methodology of LCA

According to ISO standards [55, 56], general methodological framework of LCA has four components. These components are described below:

- Goal and scope definition
- Inventory analysis (LCI)
- Impact assessment (LCIA)
- Interpretation

These four components are associated each other and generate the systematic framework of LCA. The relationship between components is shown in Figure 2.33.

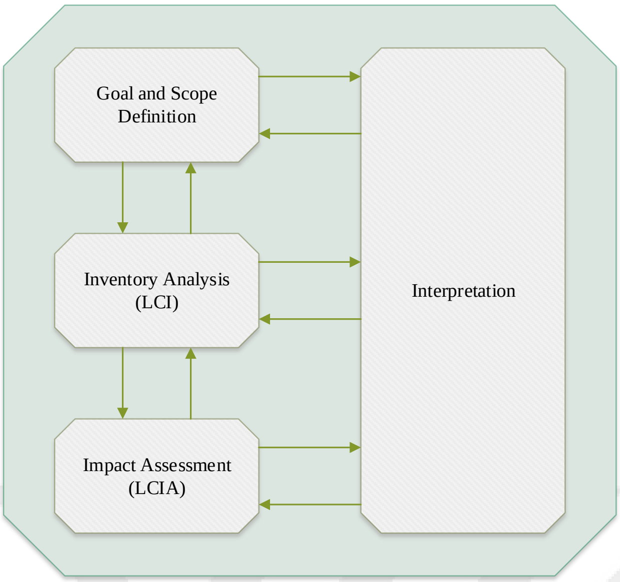


Figure 2.33 : The framework of the LCA [369].

2.11.2.1 Goal and scope definition

The goal and scope definition is the first step of the LCA studies and one of the most critical parts during LCA studies because of having substantial effects on the results of LCA. The goal and scope definition can be changed after the results of the study.

The planned application, the purpose of the study, the desired audience and whether the study outputs are planned to applied in comparative statementd intended to be disclosed to the public have to be defined in the goal definition. The applicants who reach the goal of the LCA study should understand the aim of the study to take proper decisions about the study. Below are some examples of the goal of LCA studies [55, 56, 369, 375]:

- Comparing two or more different products which are used for the same purpose
- Comparing existing product and newly designed product
- Identifying areas, units, etc. of a product for ecolabelling

Scope definition is the part of the selection of methodology and requirements and set the borders of the LCA study. For scope definition, system boundary, functional unit, allocation procedure, impact categories, and impact assessment methods have to be defined. While LCA is an iterative method, the scope can be changed during the study [55, 56, 375].

Functional unit

The term of the functional unit indicates the numerical performance of a process for use as a reference unit. The main aim of a functional unit is to ensure a mathematical reference to for input and output data normalization. All collected data in the LCI phase are connected to the functional unit. The efficiency of a poduct, product stability and performance quality standard are the three aspects for the selection of functional unit. For the selection of the functional unit, the reference point should be defined. This reference point could be the input unit, an output unit, land usage, etc. The systems which are compared in LCA studies should be done with the same reference point [55, 56, 369, 375]. Some examples of a functional unit for biorefineries which were published in the journals are listed below:

- 1 ton feedstock
- 1 biorefinery
- 1 MJ fuel
- 1 L fuel
- 1 kg of fuel
- 1 km driving
- 1 person.km
- 1 ha of land usage

System boundary

A product system includes some unit operation processes, and the system boundary set the unit operation process which is included in LCA study. The goal, scope and system boundary should be consistent. Some examples of system boundaries are shown in Figure 2.34.

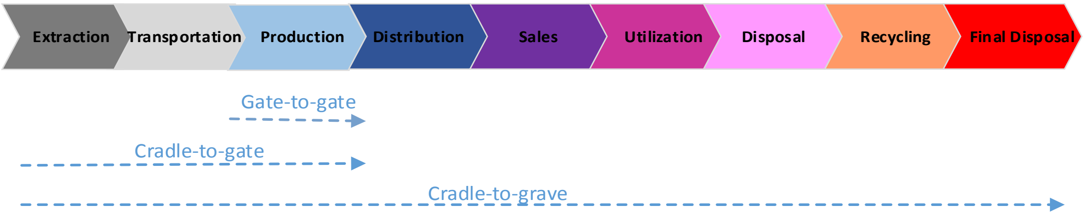


Figure 2.34 : System boundaries of LCA, adapted from [52].

Gate-to-gate approach includes only production step. It starts with the entrance of the feedstocks and ends with the producing products. Cradle-to-gate approach includes biomass cultivation, harvesting and transportation and production of the product. Cradle-to-grave approach contains every step from harvesting to final disposal. For producing corn-bioethanol, gate-to-gate approach contains corn to ethanol process only. Cradle-to-gate contains corn harvesting, land to plant transportation and corn to ethanol process. Cradle-to-grave contains corn harvesting, land to plant transportation and corn to ethanol process, plant to user transportation, user utilization, disposal, recycling, and final disposal.

While the system boundary set, any stages or process are not omitted in the system boundary. If the process or stage have not to effect on LCA, the omission can be acceptable. Generally, the wastewater treatment system is omitted during the identifying system boundary [55, 56, 369, 375].

Allocation procedure

The term of allocation defines splitting the inlet and outlet flows of a process or a processing system between the product systems study and one or more product systems [55, 56]. If a system includes products, coproducts, recycle systems or reuse streams, the allocation procedure should be applied. While the different products exist in LCA study, the input and output flows shall be split according to defined ISO Standards allocation procedure. The total of allocated flows must be equal to flow before allocation. Several allocation approaches are available, and the allocation method selection could be made according to process requirements. Partitioning methods, system expansion, and hybrid methods are the most common allocation procedure.

If it is possible, the allocation should be made towards physical properties such as mass and energy content. While physical parameters do not exist, economic based allocation could be used for the allocation procedure. However, while economic parameters are varied depending on time and region, usage of economic parameters are not often used. Production of alternative or conventional co-products are attached to the biorefinery and expanding the biorefinery system and avoided allocation. This method is called system expansion [376].

Impact categories and impact assessment methods

The aim of the selection of impact categories is defining the environmental categories and presenting the results in this term of environmental hazard categories. According to ISO 14044, abiotic resources, biotic resources, land use, global warming/climate change, stratospheric ozone depletion, human toxicity, ecotoxicity, photochemical oxidant formation, acidification, land use, water use, and eutrophication are the impact categories of LCA studies. Global warming, ozone depletion, and resource depletion have global impacts. Global warming causes polar melt; forest lost, seasonal changes, wind and ocean pattern changes; ozone depletion increases ultraviolet radiation, and resource depletion reduces the resources. Photochemical smog and acidification have regional impacts. The effects of the photochemical smog are decreasing visibility, causing eye irritation and health damage. Also, acidification causes corrosions on buildings, and harmful effects on human health, vegetation or plantation, and soil. Lastly, human health, terrestrial toxicity, aquatic toxicity, eutrophication, land use, and water use have local impacts. Human health increases diseases and deaths. Terrestrial toxicity reduces productivity and biodiversity. Aquatic toxicity reduces biodiversity and lives in seas and oceans. Eutrophication causes excessive plant growth and oxygen depletion. Land use and water use causes reducing landfill areas and decreasing underground, ground and surface water resources boundary [55, 56, 369, 375].

The impact categories are commented under impact assessment methods. Different impact assessment methods are formulated and applied in life cycle impact assessment (LCIA) calculations such as CML, Eco-indicator, EPS, Ecotax, LIME, ReCiPe, etc. Generally, LCIA methods are divided into two groups such as problem-oriented/midpoint method and damage-oriented/endpoint method. Problem-oriented methods classify the flow into environmental problems. Some examples of midpoint categories are climate change, eutrophication, land use, acidification, human and ecotoxicity, depletion of stratospheric ozone and biotic sources. The damage-oriented method categorizes the endpoint impacts such as impacts on human health, impacts of ecosystem and impacts of resource availability. In the LCA studies, generally, CML [377-379] or ReCiPe [118, 378, 380-384] methods are selected for midpoint method and ReCiPe [377, 385, 386] is selected for endpoint method [387-389]. ReCiPe endpoint method is replaced Eco-indicator99, recently.

2.11.2.2 Inventory analysis

The LCI analysis bunch the data collection and calculation procedure and quantitate inlet and outlet data through the unit process or blocks [390]. According to ISO 14044 [56], the main steps of LCI are;

- Preparation for data collection
- Data collection
- Data validation
- Data to unit process relation
- Functional unit and data relation
- Aggregation of data

LCI is presented as a table and shows the quantity of each step such as inputs and outputs from or to environment and technosphere. The unit of the results is a reduced flow rate per functional unit. These data can be collected from experiments, literature, databases, reports, pilot studies, existing plants, process simulators and LCA databases from LCA software [60]. While being an iterative study, goal and scope definition could be revised according to LCI results [390].

Selection of LCI modeling for LCA studies should be consistent with goal and scope. Traditionally, the LCA models could be consequential modeling or attributional modeling. In the LCA studies, attributional LCI modeling (ALCI) and consequential LCI modeling (CLCI) approaches are used. The physical flows are constant during the whole life cycle in ALCI, while the flows varied depend on the environment in CLCI [371, 391, 392]. The principal variations are presented in Table 2.12.

2.11.2.3 Impact assessment

Aim of the life cycle impact assessment (LCIA) realizing and estimating the quantity and importance of the possible effects on the environment for a product or process all through the life cycle. The difference of the LCIA from other assessment methods such as risk assessment, environmental impact assessment, and environmental performance evaluation is its functional unit based approach. LCIA phase should be well structured and synchronized with other steps of LCA study [55, 56]. The elements of the LCIA are presented in Figure 2.35.

Table 2.12 : Key variations between ACLI and CLCI modeling [393-395].

	ACLI	CLCI
Aim	To determine the whole emissions from process and material flows which are used in the LCA study	To determine the variations in the total emissions as impacts of a marginal variation in the LCA study
Application	The emissions are directly engaged with LCA	To enlighten the decision makers and consumers how policies and decisions affect total gas emissions
System Boundary	Includes material flows and processes which are directly engaged with production, consumption, and disposal of a product	The effects of marginal variation of product output and value are directly or indirectly on material flows and processes
Data	Average data	Marginal data
Market Impacts	The impacts of the market are not regarded	The impacts of the market are regarded
Allocation Methods	The emissions of co-products are calculated mass based, economic based or energy based allocation method	The emissions of co-products are calculated by system expansion

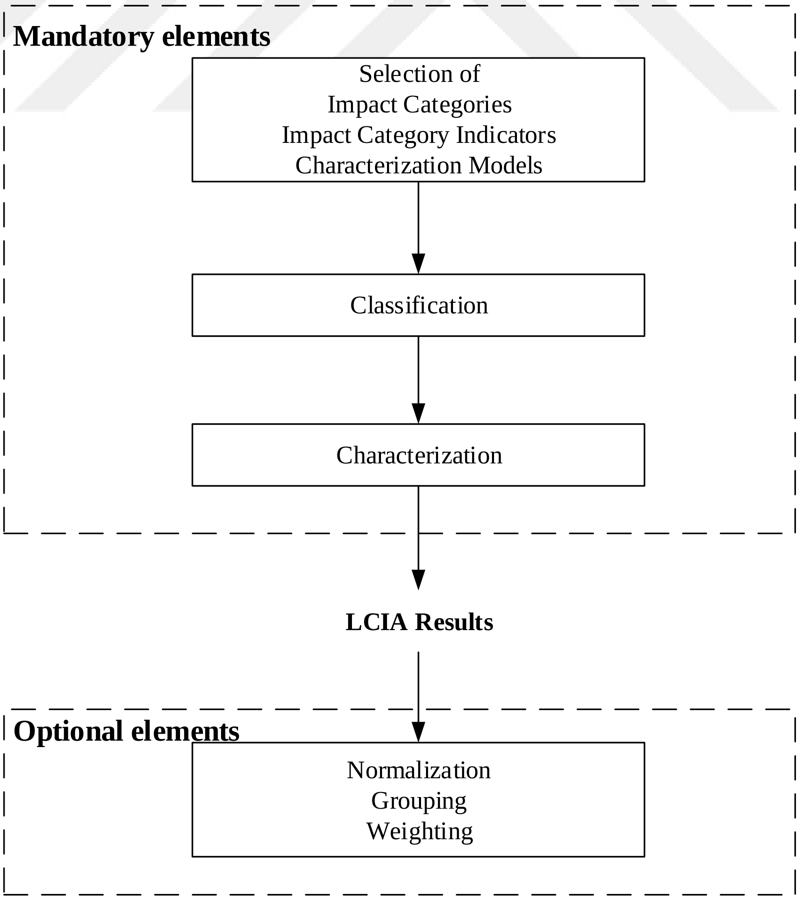


Figure 2.35 : The elements of LCIA, adapted from [55, 56].

The mandatory elements of LCIA phase are a choise of impact categories, classification, and characterization. On the other hand, normalization, grouping, and weighting are the optional elements of LCIA.

Choises of impact categories, category indicators, and characterization models are the beginning mandatory elements of LCIA. This selection must be compatible with a defined goal and scope. Also, selected LCIA indicator methods demonstrate the purpose of the study. For example, fossil fuel usage or land usage is determined as goals of the study; selected indicators have to reveal these results. Therefore, the selected impact methods should be well known and most appropriate to the goal and scope definition [396].

Classification is the second mandatory steps which were defined by ISO 14040 and ISO14044 [55, 56]. In this step, each emission is classified into the midpoint indicator groups. One emission either in a group or more than one group. Table 2.13 indicates the midpoint indicator classification of emissions.

Characterization is the magnitude determination of the effects of each inventory discharge, and the results of the midpoint indicator are characterization factors which employ to the inventory flows to determine an aggregate category indicator. For example, “Climate change” indicator results are given with different GHG emissions such as CO_2, CH_4, and N_2O, etc. However, each GHG is expressed within $kgCO_{2eq}$ /functional unit according to characterization factor is global warming potential (GWP) which was developed by the International Intergovernmental Panel on Climate Change (IPCC) [390]. Classification and characterization steps are automatically prepared by LCA software. Thus, users are not defined by each group manually. However, users can also create a new classification group manually [396]. Optional steps of LCIA is defined as normalization, grouping, and weighting according to ISO 14040 and ISO14044 [55, 56]. In normalization step, each midpoint category results are divided by a reference value such as global, regional, national or local values, per capita basis or equivalent measurements. The normalization step aims to present the midpoint indicator results with a comparable unit. Optionally, category indicators are categorized into groups in the grouping step. These groups could be local, global or regional groups. Besides, these groups could be ordered as low, medium or high priority. These groups should be determined in goal definition.

Table 2.13 : Example midpoint indicator classification of emissions, adapted from [396, 397].

Impact category	Scale	Examples of LCI data (i.e., classification
Global Warming	Global	Carbon dioxide (CO_2), carbon monoxide (CO), nitrous oxide (N_2O), methane (CH_4), halons, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), methyl bromide (CH_3Br), Tetrachloromethane (CCl_4), 1,1,1-Trichloroethane (CCl_3CH_3)
Stratospheric Ozone Depletion	Global	Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, methyl bromide (CH_3Br), tetrachloromethane (CCl_4), 1,1,1-trichloroethane (CCl_3CH_3)
Acidification	Regional, Local	Sulfur oxides (SO_x), nitrogen oxides (NO_x), hydrochloric acid (HCl), hydrofluoric acid (HF), ammonia (NH_4), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), hydrogen sulfide (H_2S)
Eutrophication	Local	Phosphate (PO_4), nitrogen oxide (NO), nitrogen dioxide (NO_2), nitrates, ammonia (NH_4)
Photochemical Smog	Local	Non-methane hydrocarbon (NMHC)
Terrestrial Toxicity	Local	Organotin compounds, metals, organic substances/persistent organic pollutants, pesticides with a reported fatal concentration to terrestrial livers
Aquatic Toxicity	Local	Organotin compounds, metals, organic substances/persistent organic pollutants, pesticides with a reported fatal concentration to aquatic livers
Human Health	Global, Regional, Local	Total releases to air, water, and soil
Resource Depletion	Global, Regional, Local	Consumed minerals and fossil fuels quantity
Land Use	Global, Regional, Local	Disposal in a landfill
Water Use	Regional, Local	Consumed water quantity

The weighting process is modifying the results of midpoint or endpoint indicator of various impact categories by using numerical factors based. It could contain an accumulation of the weighted indicator results [55, 56, 390, 396].

2.11.2.4 Interpretation

The last phase of the LCA study is an interpretation which bunch LCI analysis, LCIA and the real world together. The main aim of the interpretation is the presentation of the comprehensible results coherent with the goal and scope definition of the study. At interpretation phase, the evaluation of all outputs obtained from LCI and LCIA phases are completed, significant contributors to total emissions and hot spots in LCA are determined, conclusions are obtained, and final recommendations are presented [55, 56, 388, 390, 396].

2.11.3 Life cycle assessment softwares and SimaPro

LCA studies cover large numbers of data, calculations, and processes and all these units are bunched together. Software that develops companies determines valuable interpretation results. In this software, databases include a massive number of data to make calculations more usable and applicable. The common aim of the software is easy usage, accurate results and reducing human-made errors. Figure 2.36 shows the situation of LCA software in LCA calculation steps.

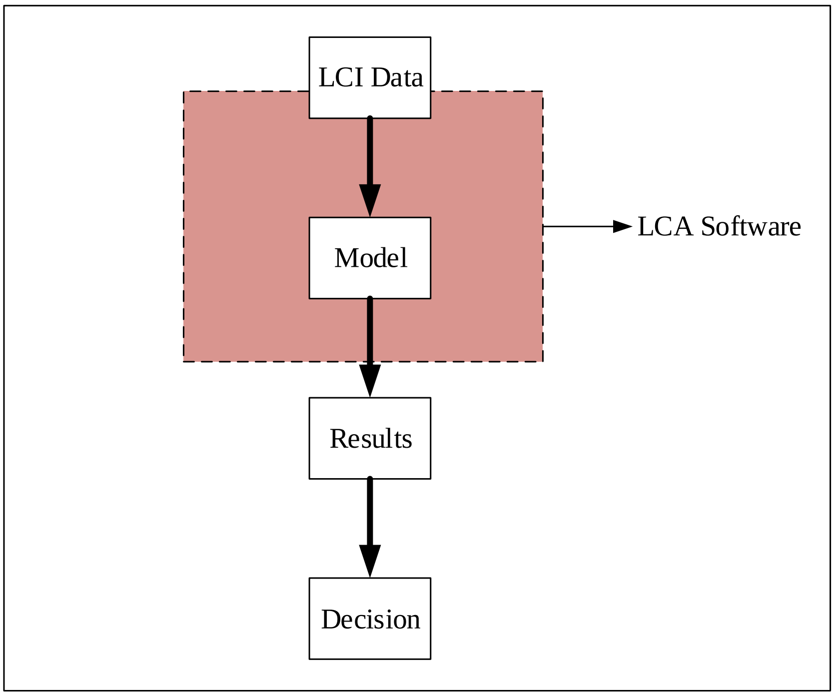


Figure 2.36 : The situation of LCA working principle, adapted from [398].

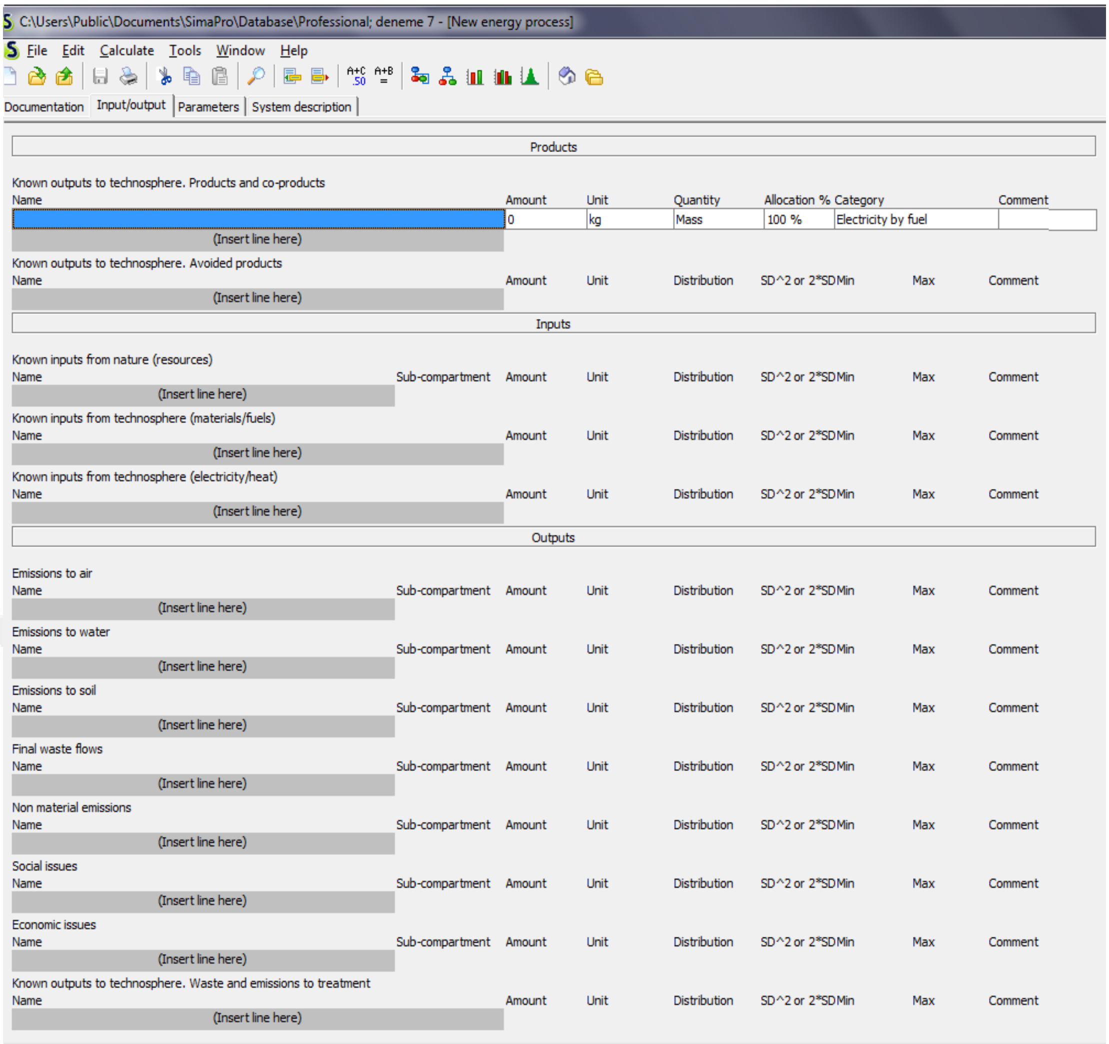
More than 20 years, companies have been developed software for LCA calculations. The most used commercial software are SimaPro[399], GaBi [400] and Umberto [401]. One other software which is available for free is OpenLCA [402]. On the worldwide, SimaPro and GaBi have the most widely market share. PE International Company developed GaBi, and PReConsultants developed SimaPro [372, 398]. In literature, the remarkable number of papers that in the prestigious journals used SimaPro software. In this thesis, the license of SimaPro7 Analyst (Ph.D.) 7.2.4 version is used for LCA calculations. SimaPro Analyst version contains all functions that the user need. The structure and interface of SimaPro software is presented below;

- LCA Wizards
- Goal and Scope
  - Description
  - Libraries
  - Data Quality Indicators (DQI) Requirements
- Inventory
  - Processes
  - Product stages
  - System descriptions
  - Waste types
  - Parameters
- Impact Assessment
  - Methods
  - Calculation setups
- Interpretation
  - Interpretation
  - Document links
- General Data
  - Literature references
  - DQI weighing
  - Substances
  - Units
  - Quantities
  - Images

LCA Wizards section presents easy ways for users to set up a new model. It also includes some examples of learning. Goal and Scope section includes “Description”, “Libraries” and “DQI Requirements” subsections. Description subsection includes several numbers of the text field. These fields are required for documentation of LCA studies. Name of the project, date, author, goal, functional unit, reference flows are some example fields that are in this subsection. One other section is “Libraries” and contains databases and methods. The database and method selection is made in this subsection. In the SimPro 7.2.4 version, the available databases are methods Dutch Input-Output Database 95, Ecoinvent system and unit processes, ELCD, EU & DK Input-Output Database, Industry data 2.0, LCA Fook DK, Methods, USA Input-Output Database 98 and USLCI. The last subsection “DQI Requirements” is the place that time, geography, type, allocation and system boundaries are defined. Consequently, the Goal and Scope section is consistent with the definition of goal and scope that stated in the ISO 14040 series [55, 56].

Inventory section includes “Process”, “Product stages”, “System descriptions”, “Waste type” and “Parameters” subsection. Data about the material, energy, transportation, processing, usage, waste scenario, and waste treatment are found in “Processes” subsection. Description, input/output, parameters and system description could be defined in this subsection. Figure 2.37 shows the appearance of an inventory data input/output page.

“Product stages” section is used to determine the product composition, product usage and disposal scenario. This section contains the assembly, life cycle, disposal scenario, disassembly, and reuse section. Product stages section is used for the combination of processes which are predefined in process subsection. System description subsection presents detailed information about the selected databases and methods. Waste types subsection is generated to defined waste types in the LCA study. Parameters subsection is the place that provides an opportunity the manual data input or calculation. Impact Assessment section contains the “Methods” and “Calculation steps” subsections. Methods are the place that available methods such as CML2, CML 2001, Eco-indicator99, ReCiPe Midpoint and Endpoint, Impact 2002+, EDIP2003, EPS 200 and EPD 2008. Calculation setup subsection permits to calculate network or tree is analyzing for a single product or compare and analyze more than one product. Interpretation section includes “Interpretation” and “Document links” subsections.



Amount: 0
Unit: kg
Quantity: Mass
Allocation %: 100 %
Category: Electricity by fuel

Figure 2.37 : The appearance of inventory data input/output page in SimaPro 7.2.4 version.

Interpretation subsection contains text field such as general observations, contribution analysis, a summary of results, conclusion, and recommendation. Document links include additional sources that provide contributions to users. General data section provides beneficial information such as literature references, DQI weighing, substances, units, quantities, and images. Consequently, a small brief of setting up a new LCA model is presented in Figure 2.38.

In SimaPro software, manual data integration is available if required LCI data exist. On the other hand, SimaPro includes databases contains more than 10000 processes. In consequence of literature reviews, the Ecoinvent database is adequate and valuable. Thus, Ecoinvent database is selected to use in this thesis.

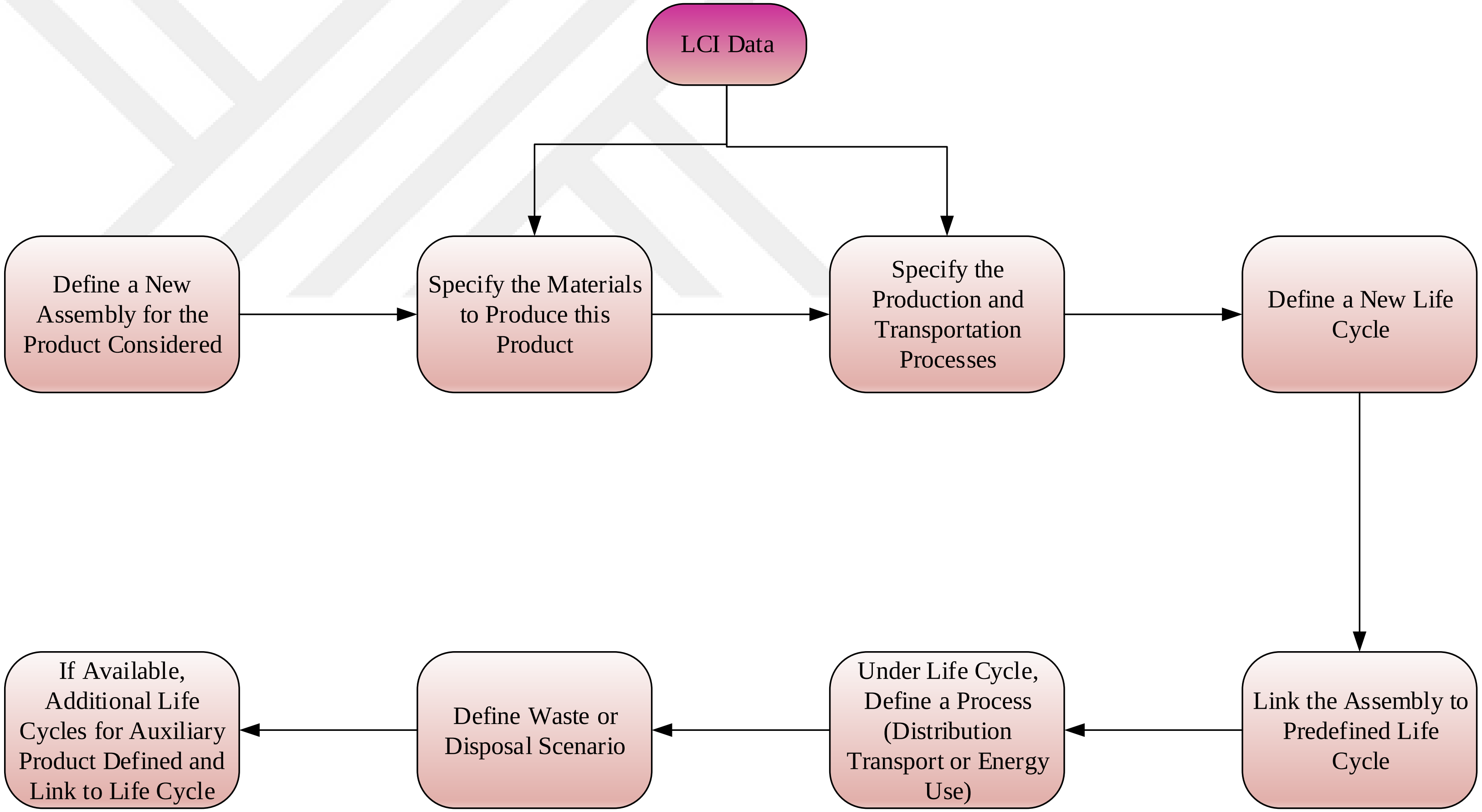


Figure 2.38 : The order of life cycle model set-up in SimaPro software, adapted from [403].

2.11.3.1 Ecoinvent database

The Ecoinvent database provides confidential, accessible LCI data such as emissions, extraction factors, processes, products, and wastes. Two versions are developed by the Ecoinvent database that are unit and system processes. Unit processes contain one process step, and the system process contains a combination of several numbers of unit processes. In SimPro software, unit processes are shown with "U", and system processes are shown with "S".

In SimaPro software, there are four variations of the dataset is applied:

1. Allocation default, U
2. Allocation default, S
3. Consequential, U
4. Consequential, S

Allocational default datasets are used in attributional modeling approach studies, and consequential datasets are used in consequential modeling approach studies. Both activity datasets and impact assessment datasets are available in the Ecoinvent database. Activity datasets describe a unit process of human activity and the interchanges between the environment and other human activities. Impact assessment datasets contain different type of impact assessment methods and their relative impact categories [404].

The geographical, temporal and technical scope is described in the dataset. Global reference activity dataset which is abbreviated as "GLO, global" targets to be proximate to the global average for the activity for the recent year. Also, non-global datasets are available in the Ecoinvent database. The rest of the world "ROW" is found to total value minus global value [404].

2.11.4 Literature review of LCA and Simapro software

Bernstad Saraiva [405] reviewed 38 research articles about system boundaries of biorefineries. The author divided the LCA of biorefineries into three types. At Type 1 LCA studies, the environmental assessment was determined under the biorefinery concept. At this type of LCA studies, different process configurations and system installation were compared. Input based functional unit was selected, and generally, no allocation method was applied. At Type 2 LCA studies, an environmental assessment was determined under one main product. This product was compared to other products. Output base functional unit and output or system expansion based allocation method was used in these studies. At Type 3 LCA studies, an environmental assessment was determined under multiple products. Their feedstocks were specific and compared with different feedstocks. Input based functional unit was selected, and the allocation method was not determined in this type of studies. According to this study, nine articles were in Type 1, 25 articles were in Type 2, and four articles were in Type 3. In this study allocation methods were also compared and four studies were chosen energy based allocation method while nine studies were economically based, three studies were mass based, and only one study was exergy based. In conclusion, if the products contained bioheat and biopower, mass based allocation method could not be used. Energy and economic based allocation methods were found more convenient.

Cherubini et al. [406] compared allocation methods for LCA of lignocellulosic biorefineries. The products were defined as bioethanol, bioheat, biopower, and phenols. System expansion, mass based, energy based, exergy based, economic based and hybrid method were used for calculations. The allocations ratios were calculated as 0.63 for bioethanol, 0.20 for bioheat, 0.13 for biopower and 0.04 for phenols under system expansion conditions. These ratios were changed as 0.99, 0, 0 and 0.01 for mass based allocation, 0.84, 0.11, 0.03 and 0.01 for energy based allocation, 0.89, 0.07, 0.03 and 0.02 for exergy based allocation, 0.91, 0.07, 0.02 and 0.01 for economic based allocation and 0.84, 0.09, 0.06 and 0.02 for hybrid allocation method. According to their statement, all allocation methods have advantages and drawbacks. For selecting allocation methods, goals and scopes were considered.

One another selection of allocation method study was made by Karka et al. [376]. Biodiesel platform biorefinery was investigating for environmental impact assessment based on gate-to-gate approaching. Four cases were studied, and mass, energy, economic based allocation method and system substitution were compared in the study. The GWP ratios of biodiesel in these 4 cases were not changed (2.20 and 1.95) based on mass and economic based allocation. However, different GWP ratios were (1.93, 2.44, 2.18, 2.55) found at system substitution. The importance of the selection of the allocation method could be defined in this study. Economic allocation gave more suitable results according to their goals and scopes.

A rapeseed biorefinery was investigated by Boldrin et al. according to energy and environmental impacts [407]. 1000 kg rapeseed were used as feedstock and rape methyl ester, and glycerine was produced in their biorefinery. Five scenarios which were technological assessment were compared such as traditional rapeseed biorefinery (S1), enzymatic transesterification (S2), straw combustion (S3), biorefinery (S4) and digestion of hydrolyzate (S5). Results were compared under global warming, terrestrial eutrophication, and acidification. The results showed that S3 had a higher impact on global warming and then S5, S4, S2, and S1 followed it, respectively. Terrestrial eutrophication and acidification results were not extraordinary change for all cases.

LCA of chemical products was done by Modahl et al. [408]. Ethanol as 96% and 99%, cellulose, lignin liquor and powder, and vanillin were produced in the biorefinery from Norwegian forests as timber and wood chips form. The system boundary was selected as cradle-to-gate, and the functional unit was set as 1 ton of each product such as (cellulose, lignin, vanillin and 1 m^3 of ethanol. The attributional LCA method was used in calculations. Because of some chemicals had lack of market price information, the economic allocation was not applied in this study. The mass allocation was selected as more appropriate and applied. The distance of transport was selected between 30 to 1502 km according to chemicals type. According to the result, oil combustion had the most impact on GWP (31%-44%). The next contributor was production and energy carriers between 21% to 27%. Then, timber, wood chips, and chemical production and transportation were followed with 17% to 28%. The GWP of ethanol 96% had lower than ethanol 99%. The only difference between the production of ethanol 96% and ethanol 99% was removing water in ethanol, and it required energy consumption and increased global warming potential. The most impact on acidification potential occurred from timber, wood chips and chemical production and transportation (38% - 53%). Oil combustion and energy carriers production and transportation were followed by 16% - 26% and 7% - 12%. The eutrophication potential was affected by most other internal processes (57% - 86%) and timber, wood chips and chemical production and transportation (5% - 23%). Generally, oil combustion, timber, wood chips, and chemical production and transportation and energy carriers production and transportation had powerful impacts on global warming potential, acidification potential, eutrophication potential, photochemical ozone creation potential, ozone depletion potential, and cumulative energy demand.

Martinez Hernandez and Ng (2017) compared acetone-butanol-ethanol (ABE) and gasification and mixed alcohols (GMA) systems [409]. The functional unit was selected as 1 GJ and for adopting co-products system expansion method was used. According to results, corn stover was the main contributor for both systems. Nutrient solvents, solvent recovery, and enzyme production were the other contributors for ABE systems. For comparing the systems, the GHG emissions were 46.2 g CO_2-eq/GJ found for ABE system while 19 g CO_2eq/GJ for GMA. Both results were lower than gasoline reference (85 g CO_2eq/GJ).

Bello et al. [118] compared different organosolv based biorefinery alternatives in terms of LCA. The cases were chosen based on products such as glucose, organosolv lignin and hemicellulose were defined as Biorefinery 1.0 (Basic biorefinery), ethanol, furfural, and organosolv lignin were defined as Biorefinery 2.0 (Advanced biorefinery) and ethanol, furfural, organosolv lignin, and acetic acid were defined as Biorefinery 2.5 (Integrating of acetic acid coproduction). The functional unit was selected feedstock base (1 t/h), transportation distance was 100 km, and volumetric allocation was stated to be a viable option for this study. According to the results, using a high amount of chemical products in acetic acid recovery and furfural recovery, they have high environmental effects. Therefore, Biorefinery 1.0 was found as the environmental case. However, this study also indicated that every new-added steps increased the number of streams, equipment, inputs from technosphere and emissions. Thus, environmental effects increase directly. These cases were not comparable according to these scenarios, and another analysis should be done.

Autohydrolysis and enzymatic hydrolysis cases were compared by Gonzales-Garcia et al. [379]. Sugar beet pulp was used for feedstock, and pectin derived oligosaccharides were produced in this study. Process yield on autohydrolysis was 20% more than enzymatic conversion. Cradle-to-gate approach was selected and showed the results of different functional unit selection. According to their study, autohydrolysis had very high impacts on environmental assessment while the functional unit was selected as feedstock base (100 kg of sugar beet pulp). However, the results had significant positive change while the functional unit was selected as economic based (1€). Therefore, the importance of the selection of the functional unit was clearly shown.

Piemonte made an LCA study for producing bioethanol and bioelectricity from wood residues such as corn and wood and compared results with fossil reference system [385]. The functional unit was selected as 1 kg of fuel and 1 kWh of electricity. The cradle-to-gate was defined as system boundary, and anhydrous ethanol dehydration was not added in a biorefinery. Surplus electricity was fed to the power grid. The allocations were calculated as 99.7% of hydrated ethanol and 0.3% of electricity for economic based allocation, 99.4% of hydrated ethanol and 0.6% of electricity for energy based allocation and 100% of hydrated ethanol and 0% of electricity for carbon content based allocation. Therefore, economic based allocation method was selected according to based on estimated market prices. The methodology of Eco-indicator 99 was selected for calculating environmental impact assessment. According to environmental impact results, biorefinery systems had lower impacts on human health and usage of resources, while a higher impact on ecosystem quality. When comparing feedstocks, biorefinery from wood had the lowest impact on human health, ecosystem quality and usage of resources. Biorefinery system from wood and corn had similar impacts on ecosystem quality and usage of resources while corn biorefinery had a lower impact on human health.

Rathnayake et al. [410] compared the feedstock effects on LCA for bioethanol production. Selected feedstocks were cassava, cane molasses, and rice straw used for producing bioethanol. However, process details were different because of producing different by-products. The functional unit was selected as 1000 L bioethanol at 99.7 % (w/w) purity. The allocation factor was set 0.64 for cassava, 0.23 for cane molasses and 0.13 for rice straw. For determining the environmental impact assessment, The ReCiPe midpoint method was used. Feedstock cultivation, transportation of feedstock to biorefinery and bioethanol conversion were in system boundary. According to results, total net bioenergy outputs were calculated as 23449 MJ for cassava, 32034 MJ for cane molasses and 25288 MJ for rice straw. Non-renewable energy requirements were 4730 MJ, 10394 MJ and 6627 MJ for these feedstocks. For comparing these feedstocks, while cassava gave the best results, rice straw gave the worst results on environmental LCA.

One another study published by Cherubini and Jungmeier [411], multiple products which were bioethanol, bioenergy, and biochemical biorefinery were compared to fossil based refinery. Switchgrass was used as feedstock in this biorefinery. The authors focused on GHG and cumulative primary energy demand in this study. According to their results, biorefineries improved N_2O emissions while reduced CO_2 and CH_4 emissions. Also, acidification and eutrophication rates were higher in biorefineries. These results caused by land use and production of switchgrass and transportation.

Cherubini and Ulgiati [412] compared feedstocks impacts such as wheat straw, corn stover, and fossil based fuel in their study. Bioethanol, bioheat, biopower, and phenol are the products, and different and complex conversion technologies were used in a biorefinery. For LCA studies, the functional unit was selected as feedstock based (477 kilo ton/year). The transportation distance was assumed as 20 km from land to pellet facility and 100 km from facility to the biorefinery. According to their results, most massive GHG emission occurred from gasoline (81% of corn stover and 84% of wheat straw), then followed electricity and heat production from natural gas (10% - 7% of corn stover and 3% - 11% of wheat straw). Also, nonrenewable energy saving is up to 80% for biorefineries. In conclusion, using crop residues are useful for environmental impacts.

A study about bioethanol and furfural production was compared in LCA from vetiver feedstock was done by Raman & Gnansounou [380]. The system boundary was defined as cradle-to-wheel for bioethanol and cradle-to-gate for furfural. Functional unit was selected as 1 km driving for bioethanol. The results were compared to a fossil reference system. According to results, the climate change was found as 0.21 kg CO_2 equivalent, and fossil depletion was 0.12 kg oil equivalent for fossil and furfural system per km, while these results were 0.0027 kg CO_2 equivalent and 0.10 kg oil equivalent for bioethanol and furfural system per km. The reduction of climate change was 0.09 kg CO_2 equivalent for fossil and furfural system per km and 0.31 kg CO_2 equivalent for bioethanol and furfural system. Fossil depletion increased 0.06 kg oil equivalent for fossil and furfural system per km and 0.04 kg oil equivalent for bioethanol and furfural system per km.

One other multi products refinery was designed by Belletante et al. [413]. Pinewood was selected as feedstock, and the input flow rate was set as 300 t/h. Outlet flow depended on the process selection. The biorefinery categories were pretreatment, hydrolysis, fermentation, butanol recovery and purification. Steam explosion method was applied at the pretreatment step. It was assumed that project life was 15 years and prices of raw materials and byproducts were not change during the whole project and cost of liquid waste treatment was set as 1 \$/m^3. In this biorefinery, inputs were set as 300 t/h pine wood, 40 t/h enzymes, 65 t/h active charcoal, 48 t/h medium pressure steam, and 714 t/h high-pressure steam. Four cases were defined and at all cases, pretreatment, hydrolysis steps were constant. At Case A, the first column was designed for acetone purification, and then ethanol and butanol distillation occurred. At Case B, azeotropic mixtures separated in the first column, then other products were distilled in two distillation columns. At Case C, only butanol and acetone were distilled in distillation columns. At Case D, the only distilled products were butanol. All cases were compared to gas stripping, liquid-liquid extraction, and pervoration as separation. At these cases, butanol production was 135, 136, 137 and 137 kt/year while acetone production was 22, 22, 22 and 0 kt/year and ethanol production was 3, 2, 0 and 0 kt/year for gas stripping. Butanol production was 91, 102, 100 and 100 kt/year for Cases A, B, C and D while acetone production was 34, 34, 35 and 0 kt/year and ethanol production was 2, 2, 0 and 0 kt/year for liquid-liquid extraction as separation. For pervaporation as separation, butanol production was 74, 76, 75 and 75 kt/year while acetone production was 18, 18, 18 and 0 kt/year and ethanol production was 1, 1, 0 and 0 kt/year. According to the results of this study, the optimal result was found at Case B with gas stipping, and the worst results were found at Case D with pervoration.

The study of Budzinski et al. [381] compared four biorefinery scenarios from beech wood. In the first scenario, annual production capacity was 41600 t/year polymer grade ethylene, 58520 t/year organosolv lignin, 90800 t/year hydrolysis lignin and 38400 t/year biomethane from 400000 t/year beech wood. In the second scenario, 58400 t/year of liquid food grade carbon dioxide was added in the first scenario. In Scenario 3, 69600 t/year anhydrous ethanol was produced instead of polymer grade ethylene. In Scenario 4, liquid food grade carbon dioxide was added in Scenario 3. The functional unit was set as 400000 t/year of feedstock and substitution method was used as the allocation method. The system boundary was determined as cradle-to-gate of the biorefinery. It was assumed that, if the fossil reference was not found for some products, the life cycle stages of nearest compounds were taken in LCA calculations. According to results, total environmental impacts were calculated as -2.33E+03 point (Pt)/year, -2.43E+03 Pt/year, -2.25E+03 Pt/year and -2.35E+03 Pt/year for Scenario 1, 2, 3 and 4. Only the results of radiation, agricultural land occupation, and urbane land occupation were greater impacts than fossil based refineries. In conclusion, Scenario 3 and 4 had better results than Scenario 1 and 2.

Levasseur et al. [414] studied the LCA of integrated forest biorefinery. Butanol, acetone, and ethanol were produced in an integrated biorefinery. Butanol was defined as a product, while ethanol and acetone were co-products. Functional unit was set as 1 kg of butanol production. The facility was assumed to 500 km distance to the city which bought chemicals from and sold butanol to costumers. The results were compared to a gasoline reference system. The best results were found for forest biorefinery with 50% of biomass cut-off system. For potential impacts on climate change, ecosystem quality and resources were originated from energy consumption and the reason for water consumption was a dilution of phenolic compounds at the detoxification step. Next, the treatment and residues of detoxification were contributed to climate change.

Parajuli et al. [415] investigated the environmental effects of bioethanol and lactic acid production from standalone and integrated biorefinery concept in their study. Both consequential (CLCA) and attributional (ALCA) LCA were determined. Economic based allocation method was chosen at ALCA while system expansion was selected at CLCA. Therefore, for Case 3 the functional unit was selected as 1 $MJ_{ethanol}$ + 1 $kg_{lactic\ acid}$. Three cases were compared which were a standalone system for bioethanol production from the wheat stream (Case 1), standalone system for lactic acid production from alfalfa (Case 2) and integrated biorefinery to produce both bioethanol and lactic acid in the same process (Case 3). These cases compared with the LCA results of global warming potential, eutrophication potential, non-renewable energy usage, and agricultural land occupation. According to their results, ALCA and CLCA had similar results for all three cases. However, GHG contributions of integrated biorefinery (Case 3) were lower than standalone systems (Case 1&2). In Case 1, GWP was occurred nearly 18% from biomass production, 8% from net energy input, 25% from enzymes, 15% from other materials and 34% from added functions. These ratios were 57% and 60% from biomass production, 2% and 19% from net energy input, 20% and 0% from enzymes, 0% and 21% from other materials and 21% and 0% from added functions for Case 2 and Case 3. In Case 3, 60% of global warming potential, 92% of eutrophication potential, 97% of nonrenewable energy usage and nearly 100% of agricultural land occupation became from biomass production. In other cases, ratios were distributed net energy input, enzyme, other materials, and added function. Biomass production was the main contributor to environmental assessment.

Cai et al. [416] were studied integrated biorefineries which produced both biofuel (biodiesel blendstock) and biochemicals (succinic acid and adipic acid). System boundaries were defined in two different ways such as biorefinery and product level. Biorefinery level LCA aimed to define total life cycle GHG emissions from the integrated biorefinery products and total reduction potential of GHG emissions for using biorefinery instead of the conventional refinery. The main aim of process level LCA was product based life cycle GHG emissions from the integrated biorefinery products and product based reduction potential of GHG emissions for using biorefinery instead of the conventional refinery. The biomass feedstock supply chain, biorefinery processes, transportation and end-use of products were contained in system boundaries. The functional unit was set as MJ for renewable diesel blendstock and US ton for succinic acid and adipic acid. In this study, 27 different allocation methods were studied and compared. For all production methods, carbon efficiency, current succinic acid price, 50% of the current succinic acid price and mass allocation were investigated. While using mass based allocation method, the same amount of energy and mass usage for the same amount of products were assumed. The energy based allocation method was not applied for this study because of biochemicals were not used as energy products. Carbon efficiency based allocation method was set as 48% for renewable diesel blend and 52% for succinic acid and 53% for biodiesel blend and 47% for adipic acid. For market value based (current chemical price) was set 16% for renewable diesel blend and 84 % for succinic acid, 27% for renewable diesel blend and 73% for adipic acid. For 50% of the current chemical price, the values were set as 28% for renewable diesel blend and 72% for succinic acid and 42% for renewable diesel blend and 58% for adipic acid. Lastly, the values of the mass allocation method were set as 28% for renewable diesel blend and 72% for succinic acid and 39% for renewable diesel blend and 61% for adipic acid. According to their comparison results, process level allocation method was found more suitable than system level allocation method. However, it required more detailed data for calculations.

Chrysikou et al. [417] published an article which produced bioethanol and succinic acid from *Phalaris aquatica L*. The evaluation LCA was under the cradle-to-gate concept. Their scenarios were compared according to GHG and energy intensity results. At Scenario 1, rainfed plantation of feedstock with a good establishment and fertilizer application nearby the biorefinery location were designed. At Scenario 2, it was similar to Scenario 1 except fertilizing. At Scenario 3, the feedstock plantation was not nearby the biorefinery. It was located at a highland plantation and fertilization were not applied. Fertilization, collection, transportation was the inputs of a chain of biomass production, and enzymes, nutrients, chemicals, and energy were selected as inputs for the biorefinery. GHG emissions were compared according to cultivation, collection, storage, transportation, biochemical conversion, electricity, and residual combustion results. For bioethanol production, the highest contribution for GHG occurred from electricity which the results were 32.29 gCO_{2eq}/MJ, 30.88 gCO_{2eq}/MJ and 30.53 gCO_{2eq}/MJ at Scenario 1,2 and 3. Then, the second contributor was biomass production with the results 4.825 gCO_{2eq}/MJ, 0.318 gCO_{2eq}/MJ and 0.207 gCO_{2eq}/MJ. Using fertilizer at Scenario 1 had a significant impact on these results. For succinic acid production, the highest contribution for GHG occurred from biomass production which the result of 127.9 gCO_{2eq}/kg at Scenario 1 while the results were 8.44 gCO_{2eq}/kg and 2.52 gCO_{2eq}/kg at Scenario 2 and 3. The biochemical conversion also had important contribution for GHG with the results of 43.11 gCO_{2eq}/kg, 40.53 gCO_{2eq}/kg and 36.03 gCO_{2eq}/kg. At both bioethanol and succinic acid production, Scenario 3 had the highest transportation impact because of locating remote area. In conclusion, Scenario 2 had more suitable results for bot bioethanol and succinic acid production.

Julio et al. [391] reviewed some articles that included design simulation and LCA of biorefineries. First of all, one product biorefineries were compared. These biorefineries were hydrocarbon biorefinery via gasification [418], bioethanol production from thermochemical process [419], biomass-derived resins [420], biodiesel production from waste vegetable oils [421], synthetic natural gas production from woody biomass [422], bioethanol production [423], butanol production in sugarcane biorefineries [424]. For biorefinery simulation, generally Aspen Plus, then Aspen HYSYS and PROII were selected. For environmental LCA, the gate-to-gate approach was selected in hydrocarbon biorefinery and bioethanol production. Other biorefineries selected cradle-to-gate approach. Generally, GWP, abiotic depletion potential (ADP), eutrophication potential (EP), acidification potential (AP), ozone depletion potential (ODP), human toxicity potential (HTP) and photochemical ozone creation potential

(POCP) were compared in these studies. One other comparison was made between multiproduct biorefineries. The functional unit was selected generally dry feedstock base in multiproduct biorefineries. However, different allocation methods were applied in biorefineries.

Zucaro et al. [425] published an article about the LCA of bioethanol fuel. Cradle-to-wheel approach was selected, and a functional unit was defined as 1 km driving. Reference system was selected as a crude oil refinery, and the product was Euro 3 gasoline. Raw resources extraction, transportation of crude oil, refinery, transportation of gasoline, supplying to service stations and usage in vehicles for 1 km were in the system boundaries in the reference system. Three cases were studied according to the diversity of feedstock such as wheat, giant reed, and fiber sorghum. These cases were also included feedstock cultivation, transportation of feedstock, second-generation biofuel conversion, transportation of ethanol, ethanol blending and distributing and usage in vehicles as E10 & E85 blends for 1 km driving. The results of environmental impacts were shown as climate change, ozone depletion, terrestrial acidification, freshwater eutrophication, marine eutrophication, photochemical oxidant formation, particulate matter formation, water depletion, and fossil fuel depletion. According to their results, most of the environmental impacts that occurred from the gasoline supply chain in E10 blends. At E10 blends, wheat straw and giant reed had similar results, while fiber sorghum had a high impact on water depletion. However, at E85 blends, terrestrial acidification, freshwater eutrophication, marine eutrophication, photochemical oxidant formation, particulate matter formation, and water depletion had higher results for fiber sorghum than wheat and giant reed. For comparing feedstocks, wheat had lower impacts than fiber sorghum and giant reed. Next, E10 and E85 bends were compared for wheat in this study and the results showed that for E85 blend had higher impacts on climate change, ozone depletion, terrestrial acidification, marine eutrophication, photochemical oxidant formation, particulate matter formation and lower impacts on freshwater eutrophication, water depletion and fossil fuel depletion.

LCA of multi-product biorefinery was studied by Farzad et al. [377]. Six different processes were compared based on their potential application, market demand, and technology. Scenarios were defined as ethanol and electricity production (Scenario 1), ethanol, lactic acid and electricity production (Scenario 2), ethanol, furfural and electricity production (Scenario 3), butanol and electricity co-production (Scenario 4), methanol and electricity production (Scenario 5) and syncrude and electricity production with Fischer-Tropsch Synthesis (FTS) (Scenario 6). In all scenarios, surplus electricity was produced and fed to the grid. LCA system boundaries contain cultivation, harvesting, and transportation of feedstock and biorefining. Cradle-to-gate approach was selected for system boundary. Functional unit was defined as a biorefinery which had 65 t/h of feedstock processing capacity. Economic allocation approach was selected for this study. Results were compared under 12 impact categories of LCA. For Scenario 1, biomass production caused maximum impacts on abiotic depletion, abiotic depletion from fossil fuels, ODP, POCP and acidification and combustion caused maximum impacts on GWP, human toxicity, freshwater toxicity, marine ecotoxicity, terrestrial ecotoxicity, and eutrophication. Similar results were seen in Scenario 2 and 4, too. Furfural production required more chemicals and evaporation had more impacts on the environment in Scenario 3. In Scenario 5 and 6, biomass production had maximum impact on all categories, except GWP and POCP.

3. ASPEN PLUS PROCESS SIMULATION OF INTEGRATED ORGANOSOLV BASED BIOREFINERY UTILIZING SESSILE OAK (*Quercus petraea*) COPPICES AND INDUSTRIAL WOOD SAWDUST

This chapter includes detailed information to develop Aspen Plus process simulation model for integrated organosolv based biorefinery (IOBB) utilizing sessile oak *(Quercus petraea)* coppices and industrial wood sawdust.
The subtopics of this chapter are:

- The Choice of Woody Biomass Sources and Sampling
- Characterization of Sessile Oak *(Quercus petraea)* Coppices and Industrial wood sawdust
- Case Studies for Integrated Organosolv Based Biorefinery Process Simulation
- Thesis Methodology
- Aspen Plus Simulation Model for Integrated Organosolv Based Biorefinery
- Validation of Aspen Plus Simulation Software

As a summary, this chapter explains firstly the detailed information about the choice of woody biomass sources, which are Sessile Oak *(Quercus petraea)* coppices and Industrial wood sawdust, for IOBB. Their laboratory analysis and characterization tables are shown. Then, case studies are defined as IOBB process simulation. Thesis methodology which is required to develop Aspen Plus process simulation is produced. Next, according to case studies, Aspen Plus simulation software is used to develop a process simulation of IOBB. All hierarchic process simulation models are explained in detail. Literature data are used to provide Aspen Plus process simulation model validation.

3.1 The Choice of Woody Biomass Source and Sampling

Two different biomass sources are decided to use for hypothetical IOBB to provide woody biomass source variety. These woody biomass sources have been chosen one from forestry biomass sources and the other from industrial wood sawdust sources.

For choosing and collecting woody biomass correctly, personal communication had done with the local authorities.

According to relations with Marmara Forest Research Institute (MFRI) [426-428], personal communications were made for choosing forestry biomass source. MFRI is an institute of GDF which is a subunit of MoFWA. The responsibility of MoFWA is management, protection, restoration and utilizing from forests. MFRI is responsible for the regions at Marmara such as Istanbul, Balıkesir, Bursa and Adapazarı [429]. It is stated that oak coppice forests in Turkey are the second biggest available forest for using at lignocellulosic biorefineries after Turkish pine forests. The oak coppice forests are 25% of the total forests in Turkey [83]. According to modern energy forestry in Turkey, the unproductive and low productive oak coppice forests are more attractive for bioenergy usage [20, 21, 430].

Bursa region has been chosen as the hypothetical pilot location for the IOBB production because of being both forested and industrial region. In Bursa, total forestry land is 486,304 hectare, and 45% of the total area is covered with forest [83]. The total area of oak coppices in Bursa is 168,210.9 hectare, and 92.6% of oak coppices (155,741.4 hectares) is defined for economical usage or commercialized forests [89]. The most common oak coppices consist of “Sessile Oak” in Bursa. Therefore, sessile oak (SOC) whose name is *Quercus petraea* (Mattuschka) Liebl. in Latin, Sapsız meşe in Turkish has been chosen as the forestry biomass source in this thesis. In Table 3.1, gives detailed information about the mass ratios of forest according to their age.

Table 3.1 : The age and mass ratios of oak forests in Bursa region [89].

Usage Ratio (%)	Usage Area (hectares)	5 Years Old (tones/h)	10 Years Old (tones/h)	15 Years Old (tones/h)	20 Years Old (tones/h)
100	155741.4	16.516	21.677	25.462	26.838
90	140167.26	14.864	19.509	22.916	24.154
80	124593.12	13.213	17.342	20.370	21.471
70	109018.98	11.561	15.174	17.823	18.787
60	93444.84	9.909	13.006	15.277	16.103
50	77870.7	8.258	10.839	12.731	13.419
40	62296.56	6.606	8.671	10.185	10.735
30	46722.42	4.955	6.503	7.639	8.051
20	31148.28	3.303	4.335	5.092	5.368
10	15574.14	1.652	2.168	2.546	2.684

Table 3.1 indicates that the mass of older oak coppices is heavier than younger oak coppices. Therefore, 20 years old oak coppices are decided to use for IOBBs. With the aid of MFRI, the oak coppice samples which are 15 individual 20 years old trees are collected from 1.3 m height from the ground in the middle of June from Vize Forest District Directorate in Kırklareli [428]. Figure 3.1 presents the picture of SOC samples.

Figure 3.1 : Sessile oak (*Quercus petraea*) samples: (a) Logs (b) Meshed wood (c) Bark.

The other woody biomass source for IOBB has been chosen industrial wood sawdust (IWS). Inegol was chosen as a pilot location because having a large furniture industry. Inegol is a small town in Bursa/Turkey. According to the Turkish Statistical Institute in 2014, populations of Bursa and Inegol are 2.787.539 and 242.232 people. The total area of Inegol is 1006 km^{2,} and the population is mostly live in the city center. The main economy depends on furniture manufacturing, and Inegol satisfies 1% of Turkey’s total export, 10% of Turkey’s furniture export and 40% of Turkey’s furniture demand. Approximately, 2500 small scale furniture manufacturer and 350 large scale furniture factory established in Inegol. Even the manufacturer which has the smallest capacity has 20000 m^2 covered area. Because of all this reason, Inegol was chosen as a case study region. For furniture manufacturing, nearly thirty types of wood are used, and the more convenient are beech tree (*Fagus sylvatica*), an oak tree (Q*uercus L*.), walnut tree (*Juglans regia*), pine tree (*Pinus sylvestris*) and fir tree (*Abies alba*). Before furniture manufacturing, these woods have treated some process in timber manufacturing such as physical and mechanical process [431].

First of all, logs are sprinkled with water for preventing cracking till cutting section which takes six to nine months. Then, logs are cut according to the size of customers preference, and at this point, 8-10% of wood converted to sawdust and collected into wells. This sawdust is composed IWS for IOBB [431]. In Inegol, there is 14 timber manufacturers exist in 2015. The total sawdust capacity of these manufacturers is 200 tones per month. They collect their sawdust in the wells under timber cutting section. There is no dye or adhesives are found in sawdust. In 2017, selling prices of sawdust were differed from 100 TL/tones to 300 TL/tones according to the type of wood [431].

IWS samples are collected in sawdust wells from Sulekler Forestry Products Trade and Industry Inc. (Sülekler Orman Ürünleri Sanayi ve Ticaret A.Ş). Figure 3.2 shows the picture of the collection steps of IWS samples.

IWS samples, each was 5 kg, were collecting in May and September, 2015. The size of industrial wood sawdust is smaller than 75 mesh size. Two samples were combined and mixed considering a quarter coning method to obtain a homogeneous mixture. Then, 1 kg sample was taken for laboratory analysis and characterization tests.

3.2 Characterization of Sessile Oak *(Quercus petraea)* Coppices and Industrial Wood Sawdust

Sample preparation (grinding and sieving) and structural analysis (holocellulose, lignin, and extractives) were done in the Forest Products Chemistry and Technology Laboratory in the Department of Forest Industry Engineering, Faculty of Forestry in Istanbul University. In the Energy Institute of TÜBİTAK, Marmara Research Center, proximate, ultimate, and thermal analysis were done.

Figure 3.2 : Collection of industrial wood sawdust samples from Inegol region: (a) Logs (b) Cutting section (c) Sawdust wells.

High-Performance Liquid Chromatography (HPLC) sugar analysis was completed in Bursa Technical University at the Faculty of Forestry in the Department of Forest Industry Engineering. D-glucose, D-xylose, D-galactose, L-arabinose, and D-mannose sugars were detected in HPLC (Agilent) at 80 °C and 0.5 ml/min flow rate according to “NREL Determination of Structural Carbohydrates and Lignin in Biomass Laboratory Analytical Procedure” [432].

The laboratory analysis results of SOC *(Quercus petraea)* and IWS are given in Table 3.2. The methods for each characterization determination is provided in Table 3.2. Some properties such as empirical formula, H/C ratio, and O/C ratio was calculated according to ultimate analysis results. Stem wood results are shown in Table 3.2.

Table 3.2 : Characterization of Sessile oak (*Quercus petraea*) coppice and industrial wood sawdust samples.

Woody Biomass Source	**Sessile Oak Coppice**			**Industrial Wood Sawdust**			
	Wet Basis	Air Dried Basis	Dry Basis	Wet Basis	Air Dried Basis	Dry Basis	Methods
Proximate Analysis (wt%)							
Moisture	28.81	4.02	0.0	12.77	5.64	0.0	ASTM D 7582-15
Ash	0.35	0.47	0.49	2.64	2.86	3.03	ASTM E 1755-01 (Reapp 2007)
Volatile Matter	58.72	79.18	82.49	71.26	77.09	81.69	ASTM D 7582-15
Fixed Carbon	12.12	16.33	17.02	13.33	14.41	15.28	ASTM D 3172-13
Ultimate Analysis (wt%)							
C (Carbon)		51.19			51.36		ASTM D 5373-14
H (Hydrogen)		5.83			5.59		ASTM D 5373-14
O (Oxygen)		41.90			39.36		ASTM D 3176-15
N (Nitrogen)		0.51			0.57		ASTM D 5373-14
S (Sulfur)		0.08			0.09		ASTM D 4239-14
Structural analysis (wt%)							
Holo-celluloses		82.15			89.49		[433]
Lignin		25.58			22.01		[434]
Extactives		5.43			2.06		TAPPI T 204 om
Glucan		41.8			30.1		[432]
Xylan		16.1			25.4		[432]
Galactan		1.1			16.1		[432]
Arabinan + Mannan		9.5			1.3		[432]
Total sugar		68.5			72.9		
Thermal analysis (cal/g)							
Lower Heating Value	2710	3845	4029	3623	3965	4235	ASTM D 5865-13 / ISO 1928-09
Higher Heating Value	3076	4147	4321	3796	4258	4410	ASTM D 5865-13
Molecular Properties							
Emprical Formula		$C_1H_{1.3667}O_{0.6134}N_{0.00854}S_{0.00059}$			$C_1H_{1.3153}O_{0.5788}N_{0.011}S_{0.00066}$		Calculated
Molar Weight (g/mol)		23.3196			22.7512		Calculated
H/C Molar Ratio		1.3667			1.3153		Calculated
O/C Molar Ratio		0.6134			0.5788		Calculated

3.3 Case Studies for Integrated Organosolv Based Biorefinery Process Simulation

Two different cases were determined for IOBB process simulation. These case studies are defined considering woody biomass source. CS-1 includes 5000 kg/h of SOC (*Quercus petraea)* and CS-2 includes 4500 kg/h of SOC (*Quercus petraea)* and 500 kg/h of IWS and. For determining SOC (*Quercus petraea)* quantity, economical usage ratios of oak forest in Bursa was determined and provided in Table 3.1 in Section 3.1. The forest usage was calculated as 19.56%, and 17.60% of SOC (*Quercus petraea)* forest in Bursa should be separate for IOBB usage for CS-1 and CS-2. According to personal communications, the mass flow rate was determined as 500 kg/h for all cases. Thus, the total woody biomass source is 5000 kg/h for CS-1 and CS-2. According to these ratios, the content of the feeding stream was calculated and shown in Table 3.3.

Table 3.3 : The content of feed streams at CS-1 and CS-2.

Content of Feed Streams (%)	CS-1	CS-2
Moisture	4.02	4.18
Cellulose	40.12	38.95
Xylan	15.45	16.30
Galactan	1.06	2.47
Arabinan	4.56	4.17
Mannan	4.56	4.17
Lignin	24.55	24.17
Ash	0.47	0.71
Extractives	5.21	4.88

The content of the feed stream of biomass in the simulation was determined according to Table 3.3. The ratio is calculated as 100% of each content of sessile oak for Case 1 and 90% of sessile oak and 10% of industrial biomass for Case 2 because of being only one feeding stream, and sessile oak and industrial wood sawdust is fed as a homogeneous mixture.

3.4 Thesis Methodology

Thesis methodology shows the steps which followed in the thesis. The thesis methodology is presented in Figure 3.3. Three main steps are found in the thesis methodology. The first step is the process simulation model development with Aspen Plus simulation software. In this step, the IOBB model is developed according to IOBB literature studies. Next, model validation is required to provide process reliability. For model validation, literature data is used as input in the process simulation model. Then, outputs are compared with the literature data outputs and consistency was calculated. If the consistency is not high enough, modifications were applied to provide consistency. While the consistency is in logical boundaries, the own data are used in the process simulation model.

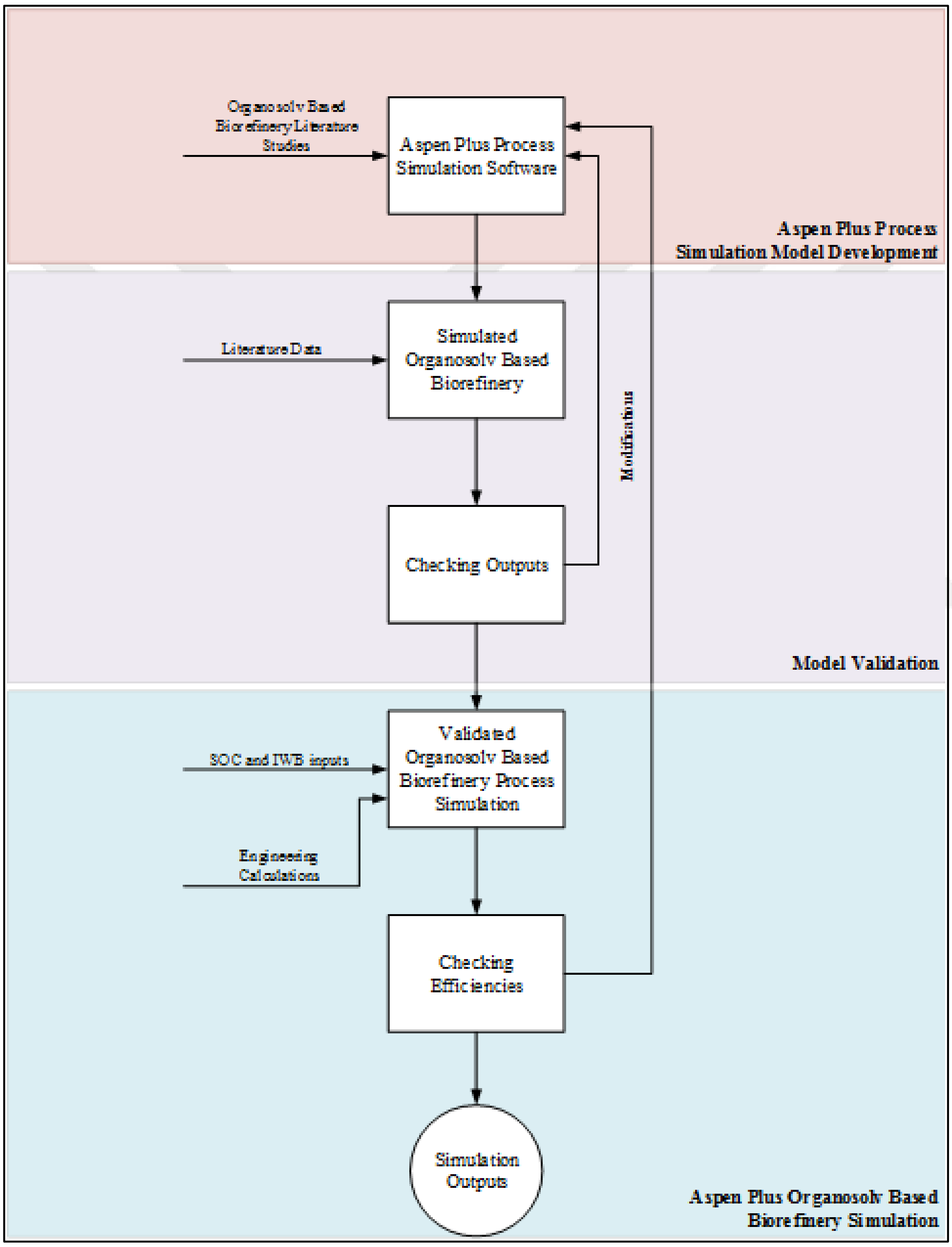


Figure 3.3 : Thesis methodology for Aspen Plus process simulation model development for IOBB.

3.5 Aspen Plus Process Simulation Model for Integrated Organosolv Based Biorefinery

This section contains detailed information about Aspen Plus process simulation model for IOBB. For process simulation, Aspen Plus V8.8 software is used for IOBB. This software was rent by Istanbul Technical University from AspenTech company, and the license rights belong to ITU, IT Department.

Some assumptions are required for model development for IOBB process simulation. These main assumptions are describing below as:

- Steady state operation
- The air content is defined as 21% of oxygen and 79% of nitrogen
- Sugars except glucose are defined as dextrose in Aspen Plus simulation software
- Annual operation time is 8600 hours
- Pressure drops in piping and equipment are negligible
- 10% of SOC samples are defined as bark
- 90% of SOC samples are without bark and grinded
- SOC and IWS samples are fed in the biorefinery as a homogeneous mixture

For developing IOBB process simulation, first of all, properties and simulation environments are defined. Then, process design is presented, and each process is implied in detail. Next, auxiliary tools such as design specifications and calculator blocks are given. Last, model validation for each process is described.

3.5.1 Properties and simulation environment

The first step of the running simulation is defining the properties and simulation environment. In Aspen Plus simulation software units, components, methods and stream class must be chosen. The detailed description of these was given below.

3.5.1.1 Units

Aspen Plus simulation software provides multiple choice to use units. In the simulation, ready packages are available for units. SET1 package is chosen for this simulation. SET1 package is arranged as temperature related units are “°C”, pressure related units are “atm” and flow related units as kg/h (mass flow), kmol/h (molar flow) and L/min (volumetric flow), power related units are “kW”, energy-related units are “J”. The result tables are generated with these unit sets. However, Aspen Plus provides another choice while input specifications.

3.5.1.2 Components

In the standard Aspen Plus databank, lignocellulosic feedstock components were not available. Thus, the physical data must be added to the simulation at first. NREL prepared a report with the title as “Development of an Aspen Plus Physical Property Database for Biofuels Components” especially for lignocellulosic ethanol production [435]. Therefore, all missing components were determined according to the NREL report. Fifty-nine components were used in the simulation and components were given in Table 3.4.

Table 3.4 : The components using in Aspen Plus simulation model for IOBB design.

Component ID	Type	Component name	Alias
Glucose	Conv.	Dextrose	C6H12O6
Cellulose	Solid		
Xylose	Conv.	Xylose	C5H10O5-D2
Xylan	Solid	Glutaric-acid	C5H8O4
Lignin	Solid		
Cellulase	Solid		
Biomass	Solid		
ZYMO	Solid		
Solible solids	Conv.	Formic acid	CH2O2
Gypsum	Solid	Formic acid	CH2O2
Acetate	Solid	Formic acid	CH2O2
Soluble Lignin	Conv.	Formic acid	CH2O2
HMF	Conv.	Formic acid	CH2O2
Arabinose	Conv.	Levulinic acid	C5H8O3-D1
Galactose	Conv.	Dextrose	C6H12O6
Mannose	Conv.	Dextrose	C6H12O6
Arabinan	Solid	Glutaric acid	C5H8O4
Mannan	Solid		
Galactan	Solid		
Glucooligosaccharides	Conv.	Dextrose	C6H12O6
Cellobiose	Conv.	Dextrose	C6H12O6
Xylan oligosaccharides	Conv.		
Tar	Solid	Glutaric acid	C5H8O4
Mannanoligosaccharides	Conv.	Dextrose	C6H12O6
Galactooligosaccharides	Conv.	Dextrose	C6H12O6
Arabinan oligosaccharides	Conv.		
Aceto oligosaccharides	Conv.	Acetic acid	C2H4O2-1
Xylitol	Conv.	Xylitol	C5H12O5

Table 3.4 (cont): The components using in Aspen Plus simulation model for IOBB design.

Extractives	Conv.		
Ash	Solid	Calcium oxide	CAO
Ethanol	Conv.	Ethanol	C2H6O-2
H_2O	Conv.	Water	H2O
Furfural	Conv.	Furfural	C5H4O2
H_2SO_4	Conv.	Sulfuric acid	H2SO4
N_2	Conv.	Nitrogen	N2
CO_2	Conv.	Carbon dioxide	CO2
O_2	Conv.	Oxygen	O2
CH_4	Conv.	Methanol	CH4
NO	Conv.	Nitric oxide	NO
NO_2	Conv.	Nitrogen dioxide	NO2
NH_3	Conv.	Ammonia	H3N
Lactic acid	Conv.	Lactic acid	C3H6O3-D1
Acetic acid	Conv.	Acetic acid	C2H4O2-1
Glycerol	Conv.	Glycerol	C3H8O3
Succinic acid	Conv.	Succinic acid	C4H6O4-2
DAP	Conv.	Diammonium phosphate	(NH4)2HPO4
Oil	Conv.	Oleic acid	C18H34O2
CSL	Conv.	Dextrose	C6H12O6
CNUTR	Conv.	Dextrose	C6H12O6
WNUTR	Conv.	Dextrose	C6H12O6
Formic acid	Conv.	Formic acid	CH2O2
Undecane	Conv.	Undecane	C11H24
SO_2	Conv.	Sulfur dioxide	O2S
H_2S	Conv.	Hydrogen sulfide	H2S
C	Solid	Carbon graphite	C
CO	Conv.	Carbon monoxide	CO
Levulinic acid	Conv.	Levulinic acid	C5H8O3-D1
Formic acid	Conv.	Formic acid	CH2O2
Soluble ash	Conv.	Calcium oxide	CAO

The components which are seen in Table 3.4, are used for IOBB design in Aspen Plus simulation software. The component IDs are the real or abbreviation of the names of components. Type is the definition if it is a conventional component (Conv.) or solid component. Component name is the name that defined in Aspen Plus Component Databases. Some components are not found in Aspen Plus Component Databases. Therefore, some of them are defined individually, and the rest of them are not defined, and similar components are used instead of them. As an example, all sugar components are defined as dextrose in the Aspen Plus simulation. The required properties for liquid and gases are T_c, P_c, ideal gas heat of formation, vapor pressure, heat capacity, the heat of vaporization and liquid density. Also, the heat of formation, heat capacity, and density are required for conventional solid components. These missing properties are found in the “Development of an Aspen Plus Physical Property Database for Biofuel Components” report which was prepared by NREL [435].

3.5.1.3 Methods

The standard NRTL method is chosen because of the ethanol distillation is required. The NRTL liquid activity coefficient model is used for the liquid phase, Redlich-Kwong-Soave (RKS) equation of state is used for vapor phase, and Henry’s law is used for the dissolved gases in this NRTL method in Aspen Plus simulation software [435].

3.5.1.4 Stream classes

The components which were used in the simulation were both solid and liquid phase. The solid phase includes components of raw material (mainly cellulose, hemicelluloses, and lignin) and the liquid phase included conventional fluids and soluble components. Thus, MIXCISLD was chosen as a stream class. The substreams were MIXED for fluids and conventional components, and CISOLID for solids and PSD were not applied in this simulation.

3.5.2 Processes

Nine processes were designed in this study to determine the IOBB. These processes were feedstock, organosolv reaction, furfural production, acetic acid recovery, enzyme production, saccharification and fermentation, distillation, cogeneration, wastewater treatment, utilities, gas collection, and storage. For being more visible and understandable, the main flowsheet is divided into three sections. The conceptual design of the biorefinery was shown in Figure 3.4. Also, Figure 3.5 presents the heat and power streams between process and Figure 3.6 indicates feedstock flows of IOBB. According to the structure of Aspen Plus simulation software, each process and units are named as hierarchy and abbreviated. “ORG” indicates organosolv pretreatment, “FURF” is furfural production, “AA” is acetic acid recovery, “ENZYME” is enzyme production, “FERM” is saccharification and fermentation, “DIST” is a distillation, “WW” is wastewater treatment and “COGEN” is cogeneration.

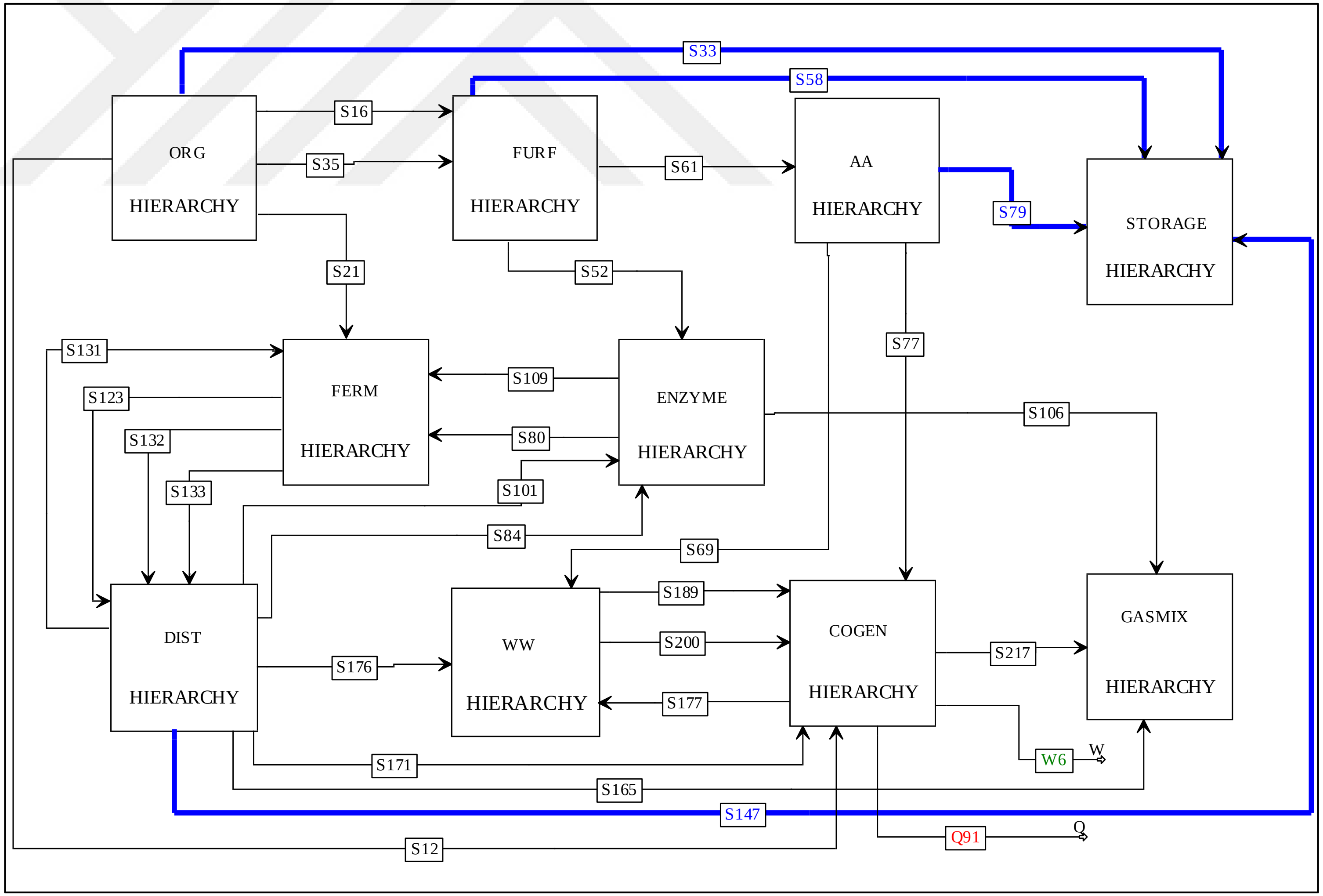


Figure 3.4 : The conceptual design of the IOBB.

The inlet and outlet streams between processes were described, and blue streams indicate product streams such as organosolv lignin, ethanol, furfural, and acetic acid. Green stream and red stream specify biopower and bioheat streams in Figure 3.4.

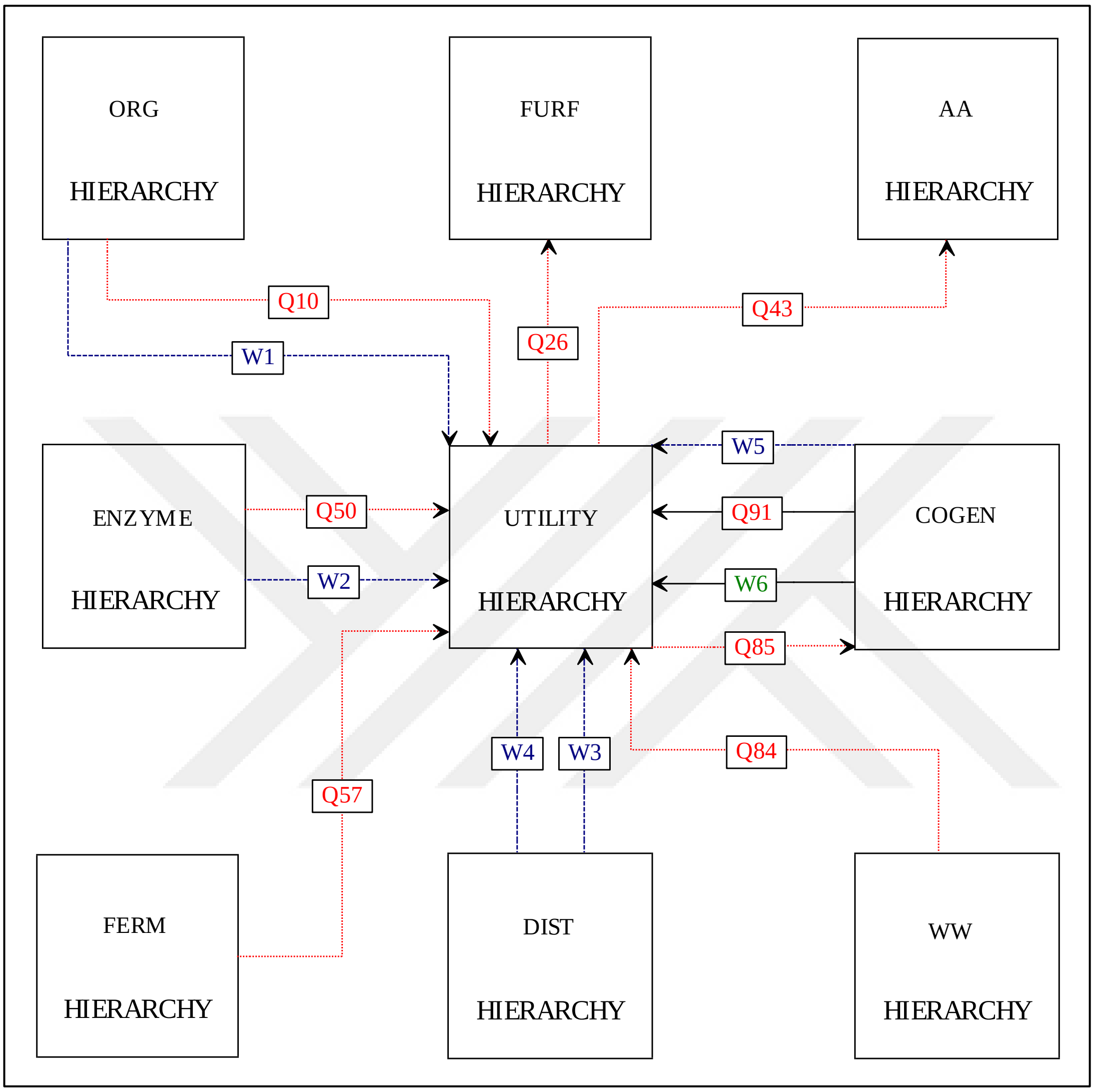


Figure 3.5 : Design of utilities in IOBB.

In Figure 3.5, heat (red) and power (blue) streams are presented between processes. The utility is the place that all produced heat and power is collected and distributed. At last, Figure 3.6 shows the feedstock requirements. Feedstocks are sent to each process and units from feedstock unit. Each process is implied individually in the next sections.

3.5.2.1 Feedstock

The feedstock process includes all purchased feedstocks, solvents and other chemicals used in IOBB. All purchased feedstocks and chemicals present in this process, firstly.

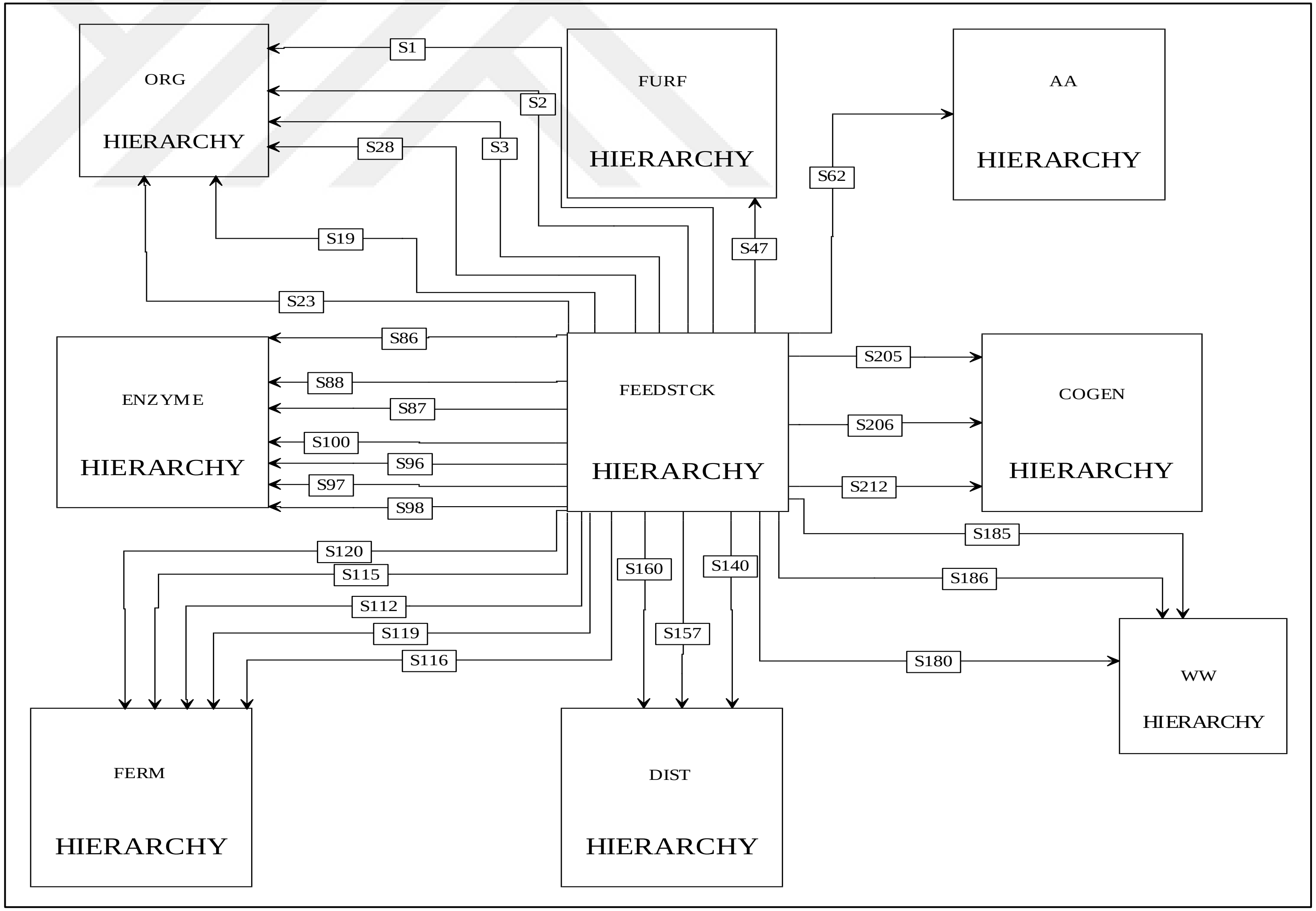


Figure 3.6 : Design of feedstock requirements in IOBB.

Then, all materials divided into the desired number of streams in this process and sent to the related process. The purchased feedstocks and chemicals are cellulase, water, ethanol, corn steep liquor (CSL), NH_3, SO_2, air, diammonium phosphate (DAP), WNUTR, bark, biomass, H_2SO_4, oil, CNUTR, and undecane. Cellulase is mixed with water sent to the fermentation process; water is sent to organosolv pretreatment, furfural production, saccharification and fermentation, and distillation process. Ethanol is mixed with water and sent to the organosolv pretreatment process. CSL is sent to enzyme production and saccharification and fermentation process. NH_3 and SO_2 mixed in a mixer and sent to enzyme production. Airstream is divided into five streams and sent to enzyme production, distillation, wastewater, and cogeneration process. DAP is sent to the fermentation process. WNUTR is used for nutrient of wastewater and sent to the wastewater process. Barks are directly sent to the cogeneration process for combustion. Biomass is defined as SOC and IWS and sent to the organosolv pretreatment process. Oil is used to prevent foaming and sent to the enzyme production process. CNUTR is nutrient for enzyme production. Thus, it is sent to the enzyme production process. Undecane is used for acetic acid extraction and sent to the acetic acid recovery process. Figure 3.7 shows the simulation of feedstock process.

3.5.2.2 Organosolv pretreatment

In the simulation, organosolv pretreatment is chosen as a pretreatment method. This process includes three steps. These are an organosolv reaction which shown as a blue box, pulp separation which presents a pink box and organosolv lignin recovery which presents with a green box. Simulation of organosolv pretreatment are shown in Figure 3.8. For simulating organosolv pretreatment conditions, two articles were followed which were written by Pan et al. (2006) and Kautto et al. (2013). The feeding ratio of lignocellulosic biomass to solvent is chosen 1:5 and this ratio is named as solid:liquid ratio (S:L). The solvent volume consists of 50% ethanol and 50% water. Catalyst loading ratio is 1.25% (w/w) on dry biomass. Solvent, biomass, and catalyst are mixed in the mixer (B1) at 25^{o}C and 1 atm, then fed in the pump (B2) to increase the pressure up to 2 MPA. The discharge pressure is set at 2 MPa and pump efficiency is determined as 85%. Pump outlet stream is sent to a heat exchanger (B3) to increase the stream temperature up to reaction temperature (190^{o}C).

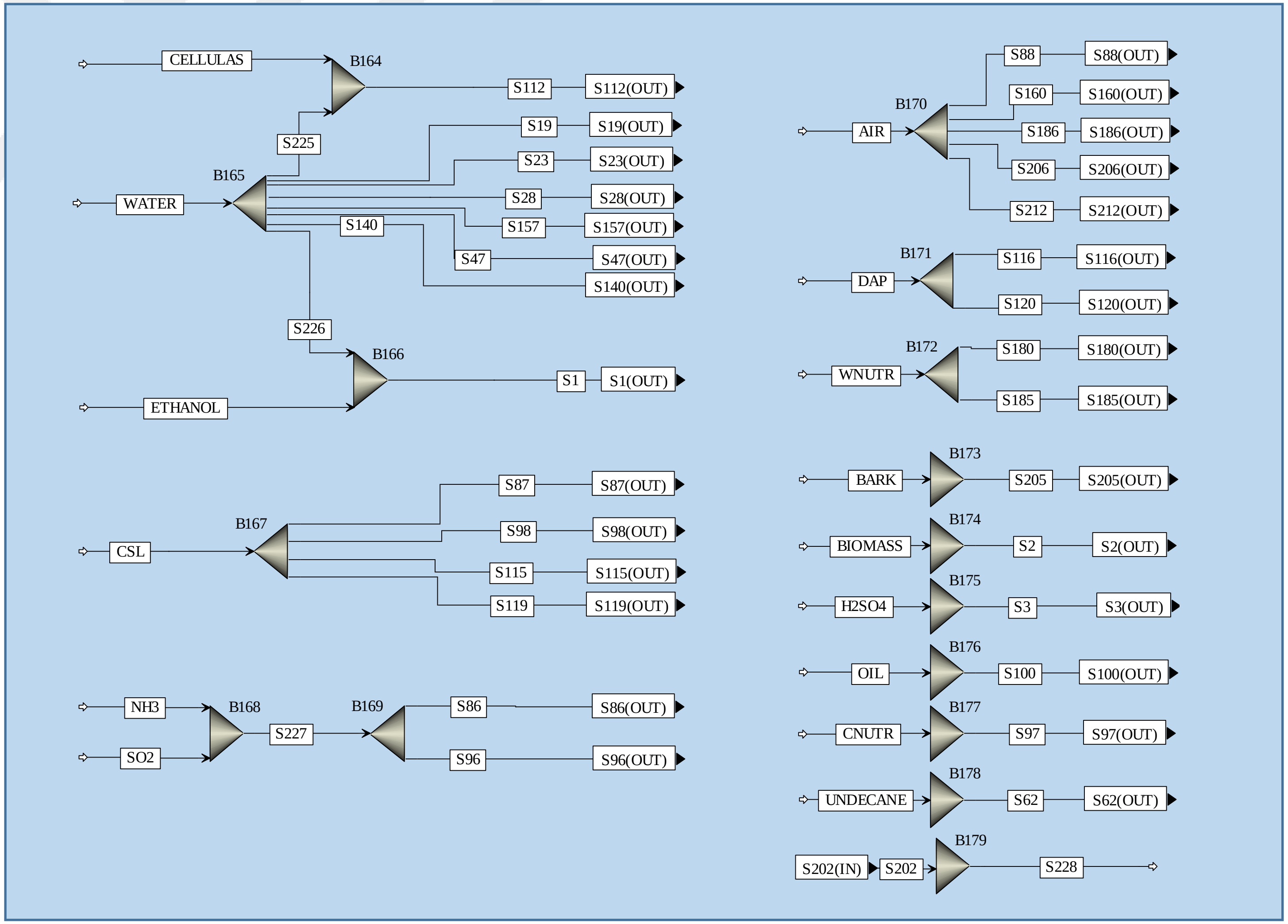


Figure 3.7 : Feedstock unit flowsheet in Aspen Plus simulation software.

The stream which reaches the reaction temperature and pressure is fed into the organosolv reactor (B4). The recycle stream (S44) is obtained from the furfural production process and fed into the "B4 reactor" for decreasing solvent consumption. "RStoic" unit operation is chosen for organosolv reaction. The reaction temperature is 190°C; pressure is 2 MPa and the retention time is 60 minutes [265, 285]. The aim of the organosolv reaction is the solubilize the lignin and separate from the wood. Thus, lignin solubilization occurs in the organosolv reactor. The reaction yields are calculated based on the experimental studies and shown in Table 3.5 [285].

Table 3.5 : Organosolv reaction yields in reactor B4.

Reaction Stoichiometry	Fraction of Conversion	Based Component
Cellulose + H_2O → Glucose	0.004535	Cellulose
Cellulose → Glucooligomers	0.00907	Cellulose
Xylan → Xylooligomers	0.30573	Xylan
Xylan + H_2O → Xylose	0.22	Xylan
Mannan → Mannooligomers	0.22857	Mannan
Mannan + H_2O → Mannose	0.11429	Mannan
Galactan → Galactooligomers	0.66	Galactan
Galactan + H_2O → Galactose	0.333	Galactan
Arabinan + H_2O → Arabinose	0.724	Arabinan
Acetate → Acetooligomers	0.4545	Acetate
Acetate → Acetic Acid	0.3636	Acetate
Lignin → Soluble Lignin	0.74	Lignin
Ash → Ash soluble	0.001	Ash
Xylan → Furfural + 2 H_2O	0.212	Xylan
Cellulose → Levulinic Acid + Formic Acid	0.01	Cellulose
Mannan → Levulinic Acid + Formic Acid	0.05	Mannan
Cellulose → HMF + 2 H_2O	0.006	Cellulose
Xylan + H_2O → Tar	0.0689	Xylan

After the organosolv reaction, a filter (B5) is required to separate the solid pulp from the liquid sugar-lignin solution. Liquid sugar-lignin fraction is heated up to 135°C at heat exchanger (B6) and is sent to the reactor (B7) for post-hydrolysis. For post-hydrolysis reaction "RStoic" unit operation is chosen.

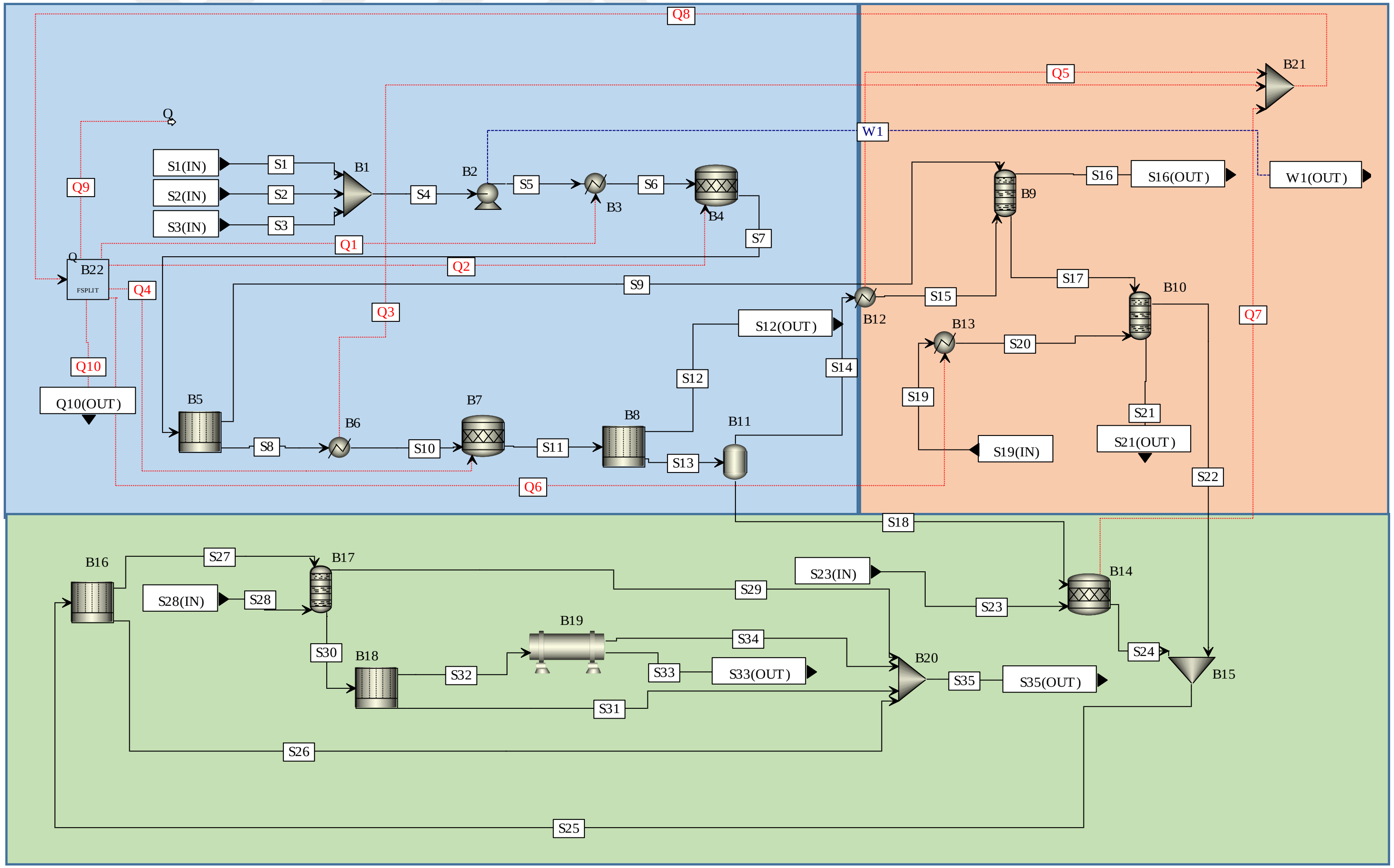


Figure 3.8 : Organosolv pretreatment process flowsheet in Aspen Plus simulation software.

The reaction temperature is 135°C; pressure is 2 MPa and the retention time is 60 minutes [265, 285]. The reaction kinetics in the post-hydrolysis reactor are shown in Table 3.6.

Table 3.6 : Organosolv post-hydrolysis reaction yields in reactor B7.

Reaction Stoichiometry	Fraction of Conversion	Based Component
Glucooligomer + H_2O → Glucose	1	Glucooligomer
Xylooligomer + H_2O → Xylose	1	Xylooligomer
Arabioligomer + H_2O → Arabinose	1	Arabioligomer
Galactooligomer + H_2O → Galactose	1	Galactooligomer
Mannooligomer + H_2O → Mannose	1	Mannooligomer
Tar (Mixed) → Tar (CISolid)	1	Tar (Mixed)
HMF + 3 H_2O → 1.2 Tar	0.35	HMF
Acetooligomer → Acetic Acid	1	Acetooligomer

Organosolv lignin separation part starts at this point. After post-hydrolysis, filter (B8) is required for separation of the solid and liquid phase. The solid phase includes unsolubilized sugars, and the liquid phase includes a solvent, water, solubilized lignin, and solubilized sugars. Solid fraction is send to the cogeneration process while the liquid fraction is fed into a flash distillation column (B11). “Flash2” unit operation is used for a flash distillation column. The working conditions of flash distillation are 0.3 bar atm and 90°C. The vapor phase is cooled at 60°C in the heat exchanger (B12) and used in ethanol washing. Pulp which is obtained after the organosolv reaction is washed with ethanol to separated unsolubilized lignin in the pulp (B9). For ethanol washing, “CCD” unit operation is chosen, and it is defined that the ethanol washing column has eight washing stages, the mixing efficiency is 0.5 and liquid to solid mass ratio is 0.25. The ethanol washing is done at 1 atm and 50°C. Then, the pulp is washed with water to the purification of pulp and to obtain lignin in the liquid phase (B10). For water washing again “CCD” column is used, and the column has 14 washing stages, the mixing efficiency is 0.5 and liquid to solid mass ratio is 0.16. Water washing pressure and the temperature are set 1 atm and 65°C. Liquid phases which obtained from flash distillation and water washing are diluted with water for organosolv lignin precipitation in a batch reactor (B14). For dilution, fresh water to organosolv lignin solution ratio is determined as 10% [285]. Precipitation occurs at 1 atm and 35°C. The stream from the precipitation reactor (S24) and water wash column (S22) are mixed in a mixer (B15) and sent to a solid-liquid separator (B16). Precipitated organosolv lignin is separated from the liquid phase with a solid separator. “Cfuge” unit operation is chosen as a solid separator. The disc model is used, and the ideal separation is set. Residual moisture is defined as 0.2. One other water wash column (B17) is required for organosolv lignin separation. For water washing, “CCD” column is used, and the column has ten washing stages, the mixing efficiency is 0.9 and liquid to solid mass ratio is 0.4. Water washing pressure and the temperature are set 1 atm and 25°C. Then, a solid-liquid separator (B18) separate the wet organosolv lignin from the liquid phase. The SSplit model is chosen for the solid-liquid separator. Wet organosolv lignin which is the solid phase is dried in the dryer (B19) at 1 atm and 105°C for 24 hours, and solid organosolv lignin is produced. The contact drier model which is 5 meters long is used in this simulation. Liquid fractions which are obtained from solid separator and dryer, mixed in a mixer (B20) and sent to saccharification process. Heat produces from equipment B6, B12, B14 and mixed in a mixer (B21). Then, heat splitter (B22) divides the heat streams for the heat necessity of B3, B4, B7, and B13. 10% of heat is assumed to be lost in this process (Q9). Surplus heat (Q10) is sent to the utility unit for using other required equipment.

3.5.2.3 Furfural production

Furfural is an undesired byproduct in the lignocellulosic biorefineries, generally. However, in this study, furfural is a valuable co-product. The ratio of furfural generation after organosolv pretreatment is 0.5%. The recovery of this amount of furfural is not economically acceptable. Therefore, a new approach is searched for to gain more furfural without inhibate the cellulose recovery. Furfural is a degradation product of xylose, xylan is mostly converted to xylose in biorefineries. A part of xylose is used for bioethanol production. However, the rest of them is sent to wastewater treatment. The study which was written by Aden et al. indicates that xylose can be converted to furfural with 75% of efficiency with the H_2SO_4 catalyst [436]. Therefore, the furfural production (xylose hydrolysis) process is attached in the simulation. Figure 3.9 shows the process of furfural production.

The furfural production process includes two sections. First one is the blue box indicates solvent recovery and the other is a pink box is furfural production and purification. Solvent recovery is required for preventing a large amount of solvent consumption. For solvent recovery, the pressure swing distillation model is used.

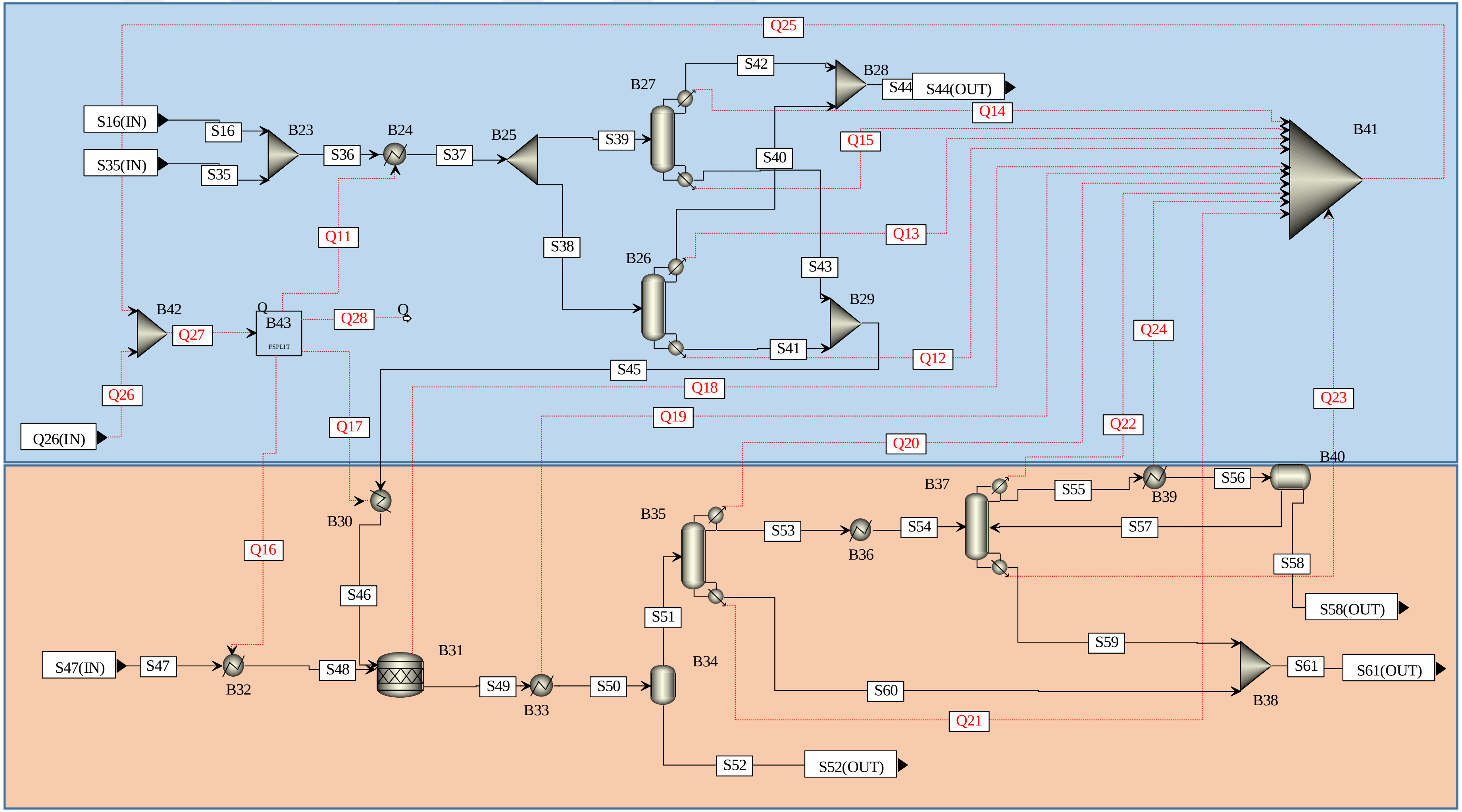


Figure 3.9 : Furfural production process for Aspen Plus process simulation software.

Solvent streams which are obtained from ethanol washing (S16) and organosolv lignin separation (S35) include a massive amount of water and ethanol and are mixed in a mixer (B23) at 1 atm. Then, the outlet stream is heated at 90°C in a heat exchanger (B24). The stream which was heated is divided into two streams with a splitter (B25). For the splitting process, “FSplit” unit operation is chosen, and stream ratios are 60% and 40% for high-pressure distillation and low-pressure distillation [285]. High-pressure distillation column (B27) is operated at 100 kPa, while low-pressure distillation column (B26) is at 18 kPa. “RadFrac” distillation column is used in the simulation for pressure swing distillation, and reflux ratio and distillate to feed ratios are set 9 and 0.32. Distillate streams which include ethanol and water are mixed (B28) and send to the organosolv reactor as solvent recycle and raffinate streams which include sugars, and other by-products are mixed in a mixer (B29) and heated at 200°C in a heat exchanger (B30). Then, this sugar-rich solution is sent to furfural production reactor (B31). Additionally, H_2SO_4 stream (S47) is heated up to 200°C in a heat exchanger (B32) and sent to furfural production reactor. Furfural reaction is shown in Equation 3.1.

$$\text{Xylose} \rightarrow \text{Furfural} + 3\ H_2O \qquad (3.1)$$

Xylose is converted to furfural with 75% of efficiency with the H_2SO_4 catalyst. At 200°C and 1 atm xylose is converted to furfural in 4 hours. When the reaction is completed, the steam is cooled at 50°C (B33) for preventing the production of degradation products. Thus, the stream includes furfural, acetic acid, and non-convertible sugars. For furfural recovery, first of all, flash distillation is required. Flash distillation aims to separate sugar solutions from furfural, water, and acetic acid. “Flash2” distillation column is chosen, and parameters are set at 130°C and 0.4 atm (B34). Sugar solution (S52) is obtained as the raffinate phase and sent to saccharification. Thus, the distillate stream includes furfural, water, and acetic acid. Furfural and water are azeotropic components, and distillation are important. For azeotropic distillation rectification column (B35) is required for purification of the furfural-water solution. Reflux ratio is set 4 and distillate to feed ratio is set 0.5. Condenser pressure is 0.2 atm and converges type is chosen azeotropic. A large amount of acetic acid and water are separate from furfural at raffinate phase. The temperature of the distillate phase is set as 97°C at heat exchanger (B36) before azeotropic distillation. Azeotropic distillation column (B37) operates at 1 atm; the reflux ratio is set 3, and the distillate rate is calculated 1200 kg/h. It has two inlet and two outlet streams. First inlet stream comes from rectification column and other inlet stream is recycled water from the decanter. Distillate stream includes 2-phase liquid (water and furfural) and due to a decanter (B40), the water stream is separated from furfural and feed in the column. Raffinate stream includes acetic acid and water. For recovering acetic acid, this stream and the other raffinate stream from rectification column are mixed (B38) and sent to acetic back acid recovery part. The heat streams (Q12 – Q15, Q18 – Q24) which are produced from equipment in furfural production process mixed in a mixer (B41). Then, the heat stream from the utilities unit (Q26) mixed in a mixer (B42). B43 heat splitter divides the heat stream for the demand of equipment. 10% of heat (Q28) is assumed to a loss in this process.

3.5.2.4 Acetic acid recovery

Acetic acid recovery is aimed for recovering acetic acid in waste solution. The extraction is the often used method for acetic acid recovery. The acetic acid recovery flowsheet is presented in Figure 3.10. Stream S61 which are obtained in furfural production process includes acetic acid and other acids such as levulinic acid, formic acid, lactic acid, and succinic acid is fed to extraction column (B44) with TOPO in undecane diluent (S62). The distribution coefficient is selected as 3 for acetic acid and TOPO concentration is set as 21.8 wt% in undecane [285]. The extraction column is set 4 stages and 100% of efficiency. The raffinate phase (S63) of the extraction column is separated and sent to combustion. Acid rich phase (S64) is heated up to 75.4°C and pressured up to 1.5 atm in B45. Then the stream is fed into the distillation column (B46) to separate acetic acid from other acid mixtures. The stage number and reflux ratio are 4 and 9.2 for the first distillation column. The distillate phase is sent to the combustion and raffinate phase is sent to another distillation column (B49). The next three distillation columns (B49, B52, and B54) have 10, 50 and 50 stages and reflux ratios are 9.2, 6.5 and 6.3. At the end of the 3rd distillation column, S79 stream is acetic acid 97% of purity. Last distillation column is designed to recover TOPO and undecane diluent. The recovered undecane diluent stream (S76) is fed to the extractor. S77 stream is included other acids and sent to the cogeneration process. Heat streams from B44, B46, B47, B49, B51, B52, B53, B54 and B 55 are collected in a heated mixer. 10% of heat is assumed to be lost in this process. The external heat stream (Q43) is added and used in B45 heater requirements.

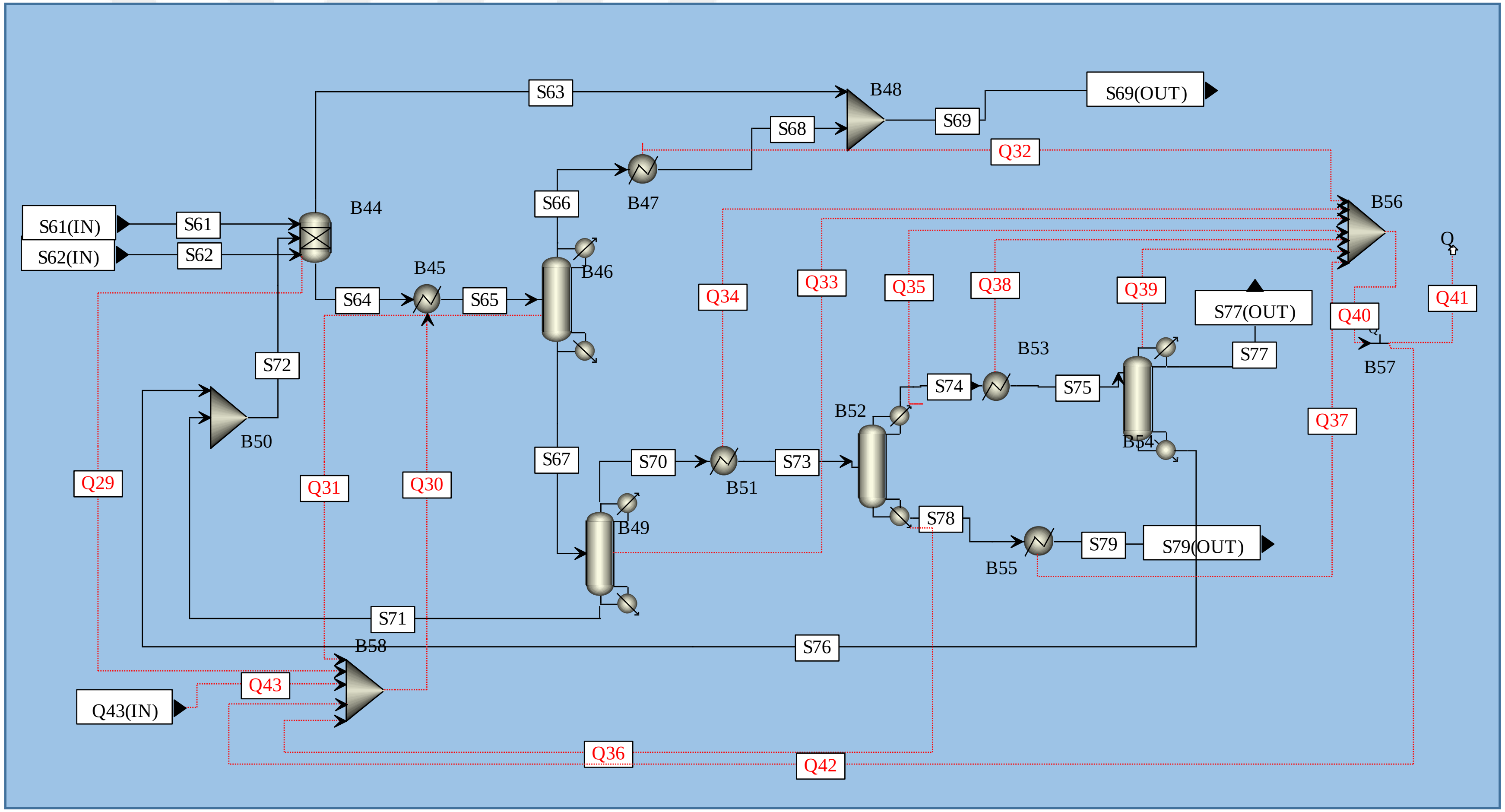


Figure 3.10 : Acetic acid recovery process for Aspen Plus process simulation software.

3.5.2.5 Enzyme production

The enzyme production process is the place that produces a suitable medium for enzyme growth, and the design of this process is shown in Figure 3.11 below. According to studies, cellulase is chosen as an enzyme for bioethanol production [436, 437]. Cellulase is a combination of different enzymes. These are endoglucanases, exoglucanases, and β-glucosidase enzymes. Endoglucanases are used to decrease the size of the polymeric cellulose structure due to attacking the cellulose fiber, randomly. Exoglucanases impacts the cellulose fibers and causes to cellulose crystallinity hydrolyzation and β-glucosidase converts cellobiose to glucose [436]. These enzymes can be produced by some white root fungus, termite guts, and bacterias, naturally. The most preferred organism for producing cellulase enzyme is "*Trichoderma reesei*" [436]. *Trichoderma reesei* is indicated as "BIOMASS" in the simulation component list and reactions and its chemical formula defined as $CH_{1.645}O_{0.445}N_{0.205}S_{0.005}$ and chemical formula of the cellulase enzyme is defined $CH_{1.57}N_{0.29}O_{0.31}S_{0.007}$. Enzyme production occurs in a two-step. First one is cellulase seed fermentation which "*Trichoderma reesei*" is growing and the other is cellulase fermentation.

First of all, the air stream is fed into the compressor (B63) to increase the pressure up to 3 atm. Then heat exchanger (B64) increase the temperature of air to 40°C. The stream splitter (B65) divide the air stream for cellulase seed fermentor and cellulase fermentor. Sugar solution (S52) is sent to stream splitter (B70), and the required amount of solution is divided. Rest of sugar solution (S80) is sent to saccharification and fermentation process. Sugar solutions (S84, S85), air (stoichiometric) (S88), CSL (1% w/w) (S87) and ammonia (7 g/L) (S86) are fed in the cellulase seed fermentation (B60). It operates at 28°C and 1 atm for 96 hours [437]. Table 3.7 shows the reactions in the cellulase seed fermentor.

Table 3.7 : Reaction stoichiometry in cellulase seed fermentor [437].

Reaction Stoichiometry
2 Glucose + 7.45217 O_2 + 0.01522 SO_2 + NH_3 →9.93478 H_2O + 7.65217 CO_2 + 4.34783 Biomass
2 Mannose + 7.45217 O_2 + 0.01522 SO_2 + NH_3 →9.93478 H_2O + 7.65217 CO_2 + 4.34783 Biomass
2 Galactose + 7.45217 O_2 + 0.01522 SO_2 + NH_3 →9.93478 H_2O + 7.65217 CO_2 + 4.34783 Biomass
2 Xylose + 5.45217 O_2 + 0.01522 SO_2 + NH_3 →7.93478 H_2O + 5.65217 CO_2 + 4.34783 Biomass
2 Arabinose + 5.45217 O_2 + 0.01522 SO_2 + NH_3 →7.93478 H_2O + 5.65217 CO_2 + 4.34783 Biomass
2 Cellulose + 7.45217 O_2 + 0.01522 SO_2 + NH_3 →7.93478 H_2O + 7.65217 CO_2 + 4.34783 Biomass
2 Mannan + 7.45217 O_2 + 0.01522 SO_2 + NH_3 →7.93478 H_2O + 7.65217 CO_2 + 4.34783 Biomass
2 Galactan + 7.45217 O_2 + 0.01522 SO_2 + NH_3 →7.93478 H_2O + 7.65217 CO_2 + 4.34783 Biomass

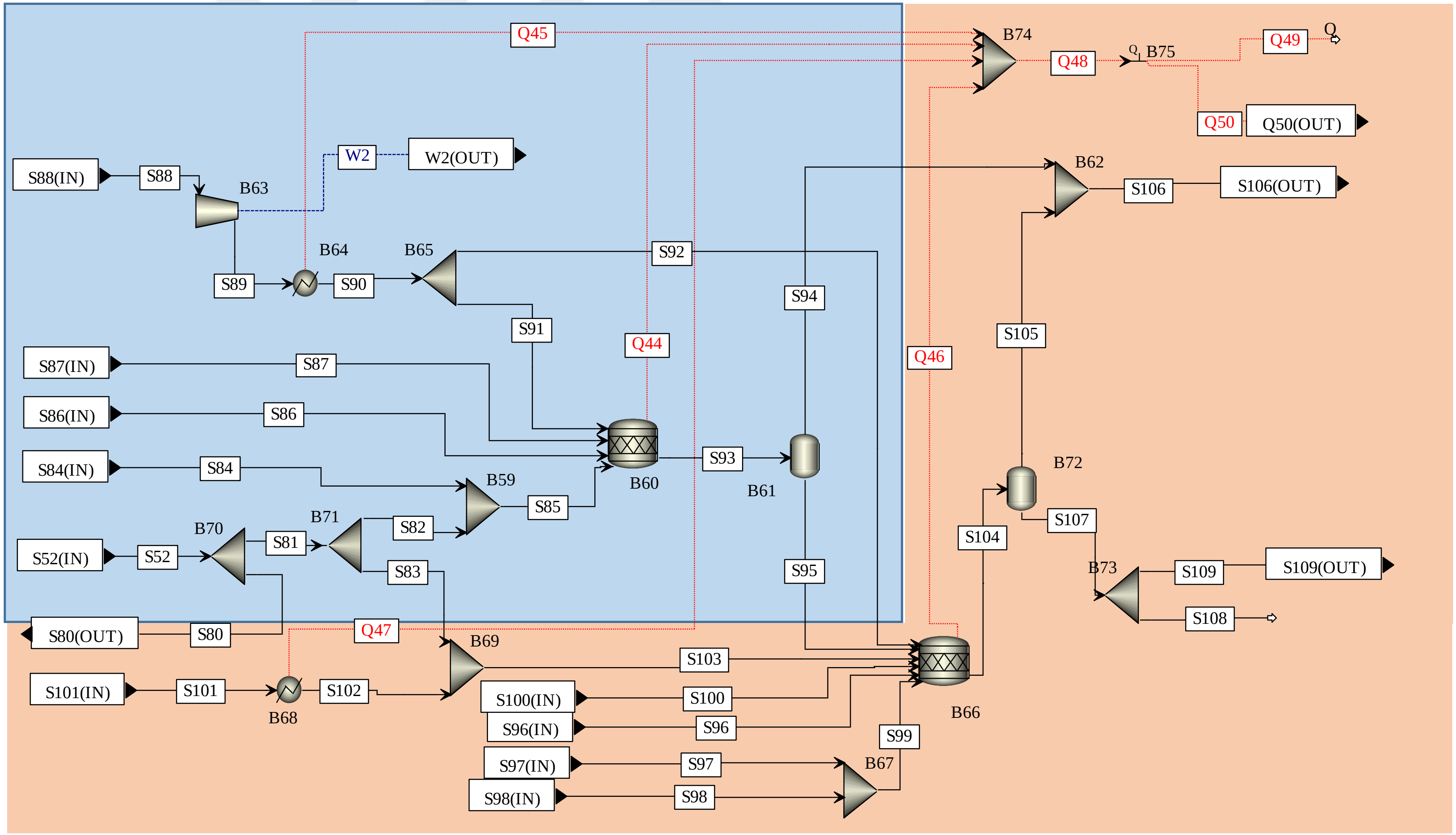


Figure 3.11 : Enzyme production process flowsheet in Aspen Plus simulation software.

The outlet stream of cellulase seed fermentor is fed into a flash distillation column (B61) to separate fermentation gases. The liquid phase which is the bottom stream of flash distillation is fed into cellulase fermentor (B66) with air (S92), CSL (S98), CNUTR (S97), ammonia (S96), antifoam (S100) streams. The feeding rates of the inlet streams are air is a stoichiometric ratio, CSL is 1% w/w, ammonia is 7 g/L, antifoam is 0.1% v/v. Antifoam is the corn oil to use to prevent foaming during fermentation and defined in simulation as oil. CNUTR is the nutrients which are required for enzyme growth and includes ammonium sulfate (1400 mg/L), potassium phosphate (2000 mg/L), magnesium sulfate (300 mg/L), calcium chloride (400 mg/L), Tween 80 (200 mg/L) [437]. The reactions which occur in the cellulase fermentor are seen in Table 3.8.

Table 3.8 : Reaction stoichiometry and a fraction of conversions in cellulase fermentor [437].

Reaction Stoichiometry	Fraction of Conversion
2 Glucose + 7.45217 O_2 + 0.01522 SO_2 + NH_3 →9.93478 H_2O + 7.65217 CO_2 + 4.34783 Biomass	0.47
2 Mannose + 7.45217 O_2 + 0.01522 SO_2 + NH_3 →9.93478 H_2O + 7.65217 CO_2 + 4.34783 Biomass	0.47
2 Galactose + 7.45217 O_2 + 0.01522 SO_2 + NH_3 →9.93478 H_2O + 7.65217 CO_2 + 4.34783 Biomass	0.47
2 Xylose + 5.45217 O_2 + 0.01522 SO_2 + NH_3 →7.93478 H_2O + 5.65217 CO_2 + 4.34783 Biomass	0.47
2 Arabinose + 5.45217 O_2 + 0.01522 SO_2 + NH_3 →7.93478 H_2O + 5.65217 CO_2 + 4.34783 Biomass	0.47
2 Glucose + 8.45862 O_2 + 0.02414 SO_2 + NH_3 →10.7931 H_2O + 8.55172 CO_2 + 3.44828 Cellulase	0.53
2 Mannose + 8.45862 O_2 + 0.02414 SO_2 + NH_3 →10.7931 H_2O + 8.55172 CO_2 + 3.44828 Cellulase	0.53
2 Galactose + 8.45862 O_2 + 0.02414 SO_2 + NH_3 →10.7931 H_2O + 8.55172 CO_2 + 3.44828 Cellulase	0.53
2 Xylose + 6.45862 O_2 + 0.02414 SO_2 + NH_3 →8.7931 H_2O + 6.55172 CO_2 + 3.44828 Cellulase	0.53
2 Arabinose + 6.45862 O_2 + 0.02414 SO_2 + NH_3 →8.7931 H_2O + 6.55172 CO_2 + 3.44828 Cellulase	0.53
2 Cellulose + 8.45862 O_2 + 0.02414 SO_2 + NH_3 →8.7931 H_2O + 8.55172 CO_2 + 3.44828 Cellulase	1
2 Mannan + 8.45862 O_2 + 0.02414 SO_2 + NH_3 →8.7931 H_2O + 8.55172 CO_2 + 3.44828 Cellulase	1
2 Galactan + 8.45862 O_2 + 0.02414 SO_2 + NH_3 →8.7931 H_2O + 8.55172 CO_2 + 3.44828 Cellulase	1

The cellulase enzyme is produced by these reactions in the cellulase fermentor at 28°C and 1.66032 atm for 96 hours [436]. A flash distillation column (B72) is required for separating fermentation gases and enzyme solution. Gas phases are collected in a mixer (B62) before sending gas collector, and enzyme solution (S109) is sent to saccharification part for hydrolysis and fermentation. The heat streams from B64 (Q45), B60 (Q44), B68 (Q47) and B66 (Q46) are mixed in a mixer (B74) and sent to heat splitter (B75). 10% of total heat (Q49) is assumed to be lost in the process, and 90% of heat (Q50) is sent to the utilities unit for using other equipment.

3.5.2.6 Saccharification and fermentation

Saccharification is the most crucial process for bioethanol production. In this process includes saccharification (blue box) and fermentation (pink box) parts. The simulation of the saccharification and fermentation process is shown in Figure 3.12.

In the first part, hydrolyzation is used to converts polymeric sugars to monomeric sugars. The main component for bioethanol production is cellulose. Cellulose is converted to glucose monomers in the hydrolyzation part. Sugar solution which is obtained from furfural recovery (S80) part and pulp stream (S21) which is the outlet stream of the organosolv reactor is mixed in a mixer (B76) at 1 atm. Then this mixture is heated at 67°C in a heat exchanger (B77). Hydrolyzation reactor (B78) is operated at 65°C and 1 atm. Cellulase is used as an enzyme in the reactor, and cellulase stream (S112) feed to the reactor. In this simulation, enzyme loading, reaction temperature and retention time are chosen as 50 FPU/ml, 65°C and 36 hours [436]. The reactions and conversion rates are shown in Table 3.9.

Table 3.9 : Reaction stoichiometry and conversion rates in the hydrolyzation reactor [436, 438].

Reactions Stoichiometry	Fraction of Conversion
Cellulose → Glucooligomer	0.04
Cellulose + 0.5 H_2O → 0.5 Cellobiose	0.012
Cellulose + H_2O → Glucose	0.9
Cellobiose + H_2O → 2 Glucose	1

The second step is fermentation after hydrolyzation/saccharification part. The stream which includes hydrolyzed sugars is cooled at 41°C in a heat exchanger (B79). Then this stream is divided into two streams by splitter (B80). The first stream which is 90% of the mainstream is sent to fermentation while another stream (10% of the mainstream) is used for seed fermentation. In the fermentation, *Z. mobilis* bacterium (ZYMO) is used as yeast for convert monomeric sugars to bioethanol, and it must be growth in a seed fermentors. Seed fermentor (B82) operates at 41°C and 1 atm for 24

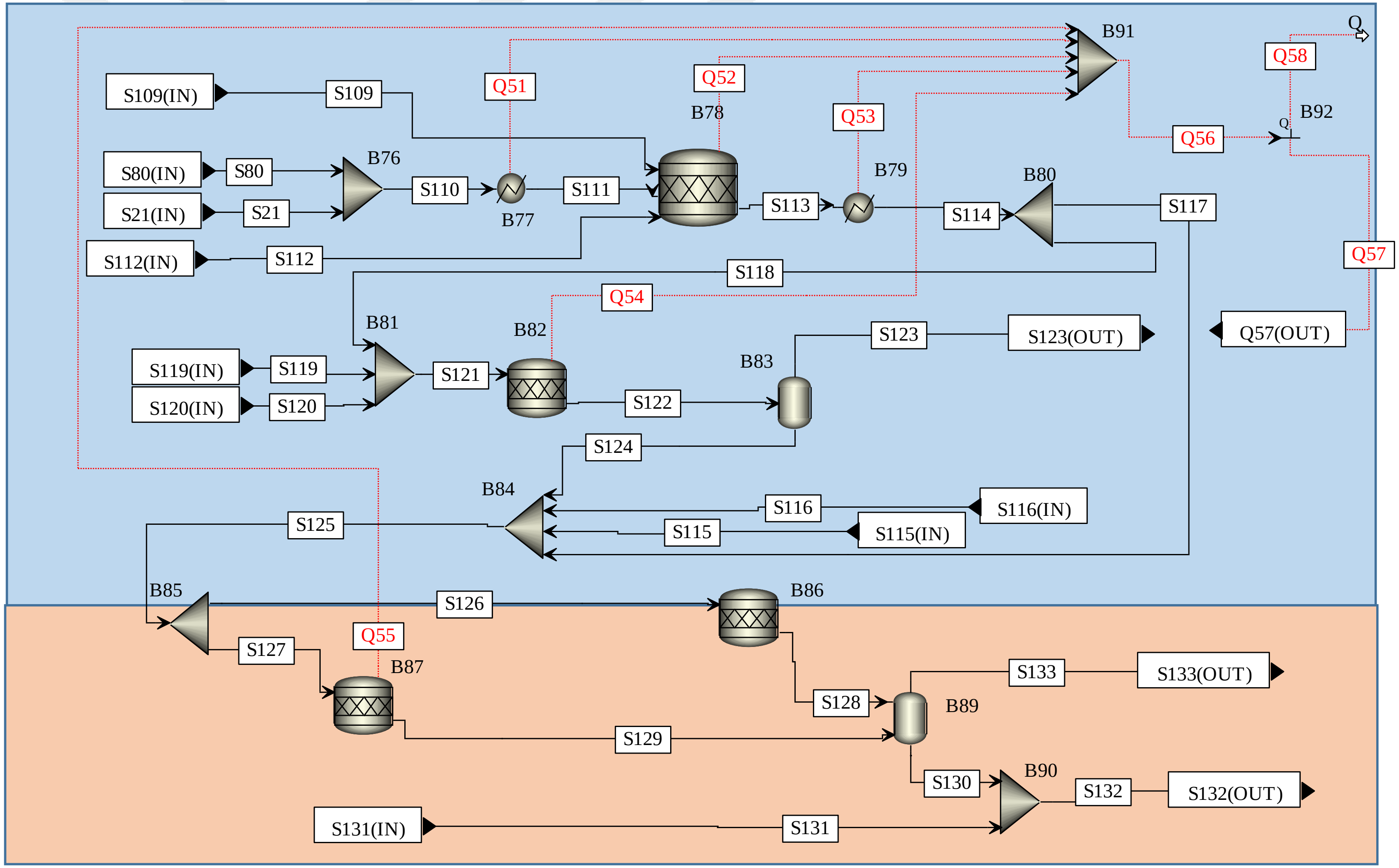


Figure 3.12 : Saccharification and fermentation process flowsheet in Aspen Plus process simulation software.

hours. 10% of the main sugar stream (S118), 0.05% of CSL (S119) and 0.67 g/L of DAP (S120) are fed in the seed fermentor (B82) [436]. The calculator blocks are used to calculate CSL, DAP and enzyme streams, and they will describe in Section 3.5.4. CSL and DAP are nitrogen nutritional source, and these are required for growing of *Z.mobilis* bacteria. After seed fermentation, flash distillation is required to separate exhaust gases. Flash distillation column (B83) is operated at 1 atm, and heat duty is set 0 cal/sec. The exhaust gas (S123) is sent to a gas collector in gasmix unit, and liquid phase (S124) is mixed with the main sugar stream in a mixer (B84). This mixer also includes CSL (S115) and DAP (S116) streams. CSL ratio is 0.25% and DAP loading is 0.33 g/ml [437]. Before the fermentation step, the stream is divided for main co-fermentation reactor and side co-fermentation reactor by a splitter (B85). The ratio of the stream is 97% and 3%. Main fermentation reactor (B87) and side fermentation reactor (B86) operate at 41°C and 1 atm [436]. The reaction stoichiometry of seed fermentation, main co-fermentation, and side co-fermentation are shown in Table 3.10 and Table 3.11.

Fermentation products are fed in a flash distillation column (B89) to separate exhaust gases. Exhaust gases (S133) are sent to the gas collector, and bottom stream (S130) which includes ethanol, water, and unconverted sugars is sent to distillation for bioethanol recovery. The heat streams which are produced by B77 (Q51), B78 (Q52), B79 (Q53), B82 (Q54) and B87 (Q55) are mixed in heat mixer (B91) and sent to heat splitter (B92). 10% of total heat (Q58) is assumed to be lost in this process, and 90% of heat (Q57) is sent to the utilities unit for using other equipment.

3.5.2.7 Distillation

Distillation is the most complicated part of bioethanol production. Due to being azeotropic components, water, and ethanol, distillation process is difficult. This process contains three parts which are wet scrubbing (blue box), distillation (pink box) and evaporation (green box) and it is shown in Figure 3.13 below. Wet scrubbing part is aimed for cleaning the exhaust gases from solid particles. Gas streams from fermentors and beer column are mixed in a mixer (B96) then washed with water to separate particles from gases. Washing column (B97) has four stages. Water is fed at the first stage (stage 1), and the gas stream is fed 4th stage. Water ratio is 40% of the

Table 3.10 : Seed Fermentor reactions and conversion rates [436].

Reaction Stoichiometry	Fraction of Conversion	
	Seed Reactor	Co-fermentation
Glucose → 2 Ethanol + 2 CO_2	0.9	0.95
Glucose + 0.04696 CSL + 0.018 DAP → 6 ZYMO + 2.4 H_2O	0.04	0.02
Glucose + 2 H_2O → 2 Glycerol + O_2	0.004	0.004
Glucose + 2 CO_2 → 2 Succinic acid + O_2	0.006	0.006
Glucose → 3 Acetic acid	0.015	0.015
Glucose → 2 Lactic acid	0.002	0.002
3 Xylose → 5 Ethanol + 5 CO_2	0.8	0.85
Xylose + 0.03913 CSL + 0.015 DAP → 5 ZYMO + 2 H_2O	0.04	0.019
3 Xylose + 5 H_2O → 5 Glycerol + 2.5 O_2	0.003	0.003
Xylose + H_2O → Xylitol + 0.5 O_2	0.046	0.046
3 Xylose + 5 CO_2 → 5 Succinic acid + 2.5 O_2	0.009	0.009
2 Xylose → 5 Acetic acid	0.014	0.014
3 Xylose → 5 Lactic acid	0.002	0.002
3 Arabinose → 5 Ethanol + 5 CO_2	0.8	0.85
Arabinose + 0.03913 CSL + 0.015 DAP → 5 ZYMO + 2 H_2O	0.04	0.019
3 Arabinose + 5 H_2O → 5 Glycerol + 2.5 O_2	0.003	0.003
3 Arabinose + 5 CO_2 → 5 Succinic acid + 2.5 O_2	0.015	0.015
2 Arabinose → 5 Acetic acid	0.014	0.014
3 Arabinose → 5 Lactic acid	0.002	0.002
Galactose → 2 Ethanol + 2 CO_2	0.8	0.85
Galactose + 0.04696 CSL + 0.018 DAP → 6 ZYMO + 2.4 H_2O	0.04	0.019
Galactose + 2 H_2O → 2 Glycerol + O_2	0.003	0.003
Galactose + 2 CO_2 → 2 Succinic acid + O_2	0.015	0.015
Galactose → 3 Acetic acid	0.014	0.014
Galactose → 2 Lactic acid	0.002	0.002
Mannose → 2 Ethanol + 2 CO_2	0.8	0.85
Mannose + 0.04696 CSL + 0.018 DAP → 6 ZYMO + 2.4 H_2O	0.04	0.019
Mannose + 2 H_2O → 2 Glycerol + O_2	0.003	0.003
Mannose + 2 CO_2 → 2 Succinic acid + O_2	0.015	0.015
Mannose → 3 Acetic acid	0.014	0.014
Mannose → 2 Lactic acid	0.002	0.002

Table 3.11 : Co-fermentation side reactions and conversion fractions [438].

Reaction Stoichiometry	Fraction of Conversion
Glucose → 2 Lactic acid	1
3 Xylose → 5 Lactic acid	1
3 Arabinose → 5 Lactic acid	1
Galactose → 2 Lactic acid	1
Mannose → 2 Lactic acid	1

gas stream, and the calculator block is used for calculating the amount of water. After the gas cleaning, the gas stream (S165) is sent to the gas collector. In distillation part,

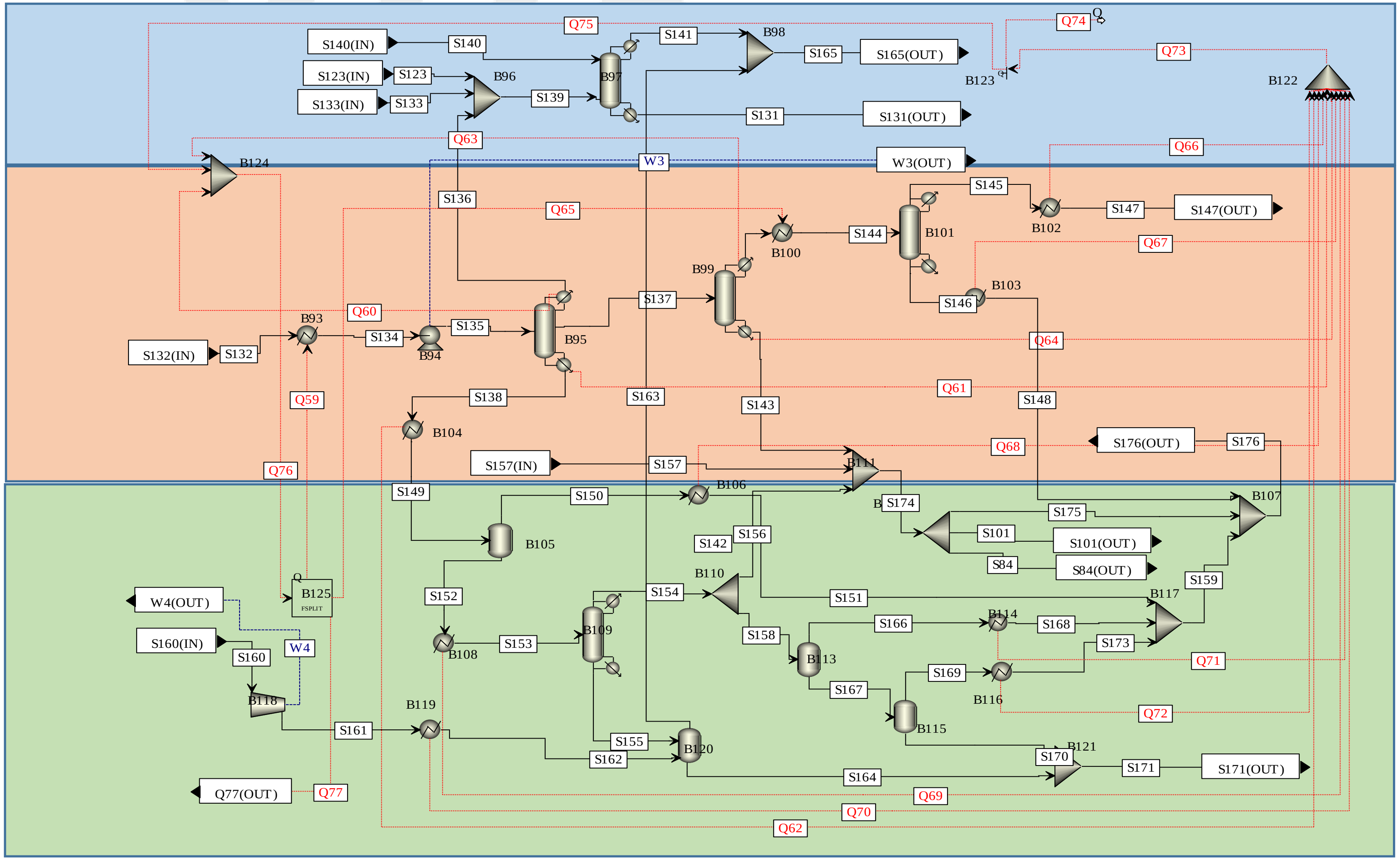


Figure 3.13 : Distillation process flowsheet in Aspen Plus process simulation software.

the solution which is outlet stream of fermentation (S132) is heated up to 100°C in a heat exchanger (B93) and sent to the compressor (B94) to increase the pressure up to 3 atm. Then, it is fed into the beer column (B95) for separating ethanol-water mixture from other components. “RadFrac” column is chosen in the simulation to design of beer column. It includes 12 stages, distillate rate, and the reflux ratio is set as the most suitable ratios. It operates at 2 atm, and the column pressure drop is defined as 0.2 atm [436]. Three outlet stream is designed for this beer column. The distillate (S13) which includes exhaust gases and vapor fraction is 1 is sent to wet scrubbing. Raffinate stream (S138) is sugar rich solution and sent to evaporation part. Another stream (S137) which obtained at the 12th stage includes mainly ethanol and water and sent to a rectification column. Retrification column (B99) is designed to separate ethanol and water from other components. It has 36 stages, converge type is strongly non-ideal liquids, distillate rate is 950 kg/h, and the reflux ratio is 1.9. It operates at 1.7 atm. The distillate stream is heated in a heat exchanger (B100) at 116°C, then sent to molecular sieve adsorption column (B101). At molecular sieve adsorption column ethanol is dehydrated for being 99.7% of purity. Then the ethanol stream is cooled at 38°C in a heat exchanger (B102) before sending storage (S147). Raffinate phase of the rectification column (S143) is mixed with the streams which will be described below in a mixer (B111) and sent to the wastewater treatment process.

The evaporation part is aimed to obtained unconverted sugars from waste solution before wastewater treatment and designed as four-effected evaporators. The inlet stream of the evaporation part is the raffinate phase is the beer column (S149). Distillate streams are evaporators mixed and sent to enzyme production and wastewater treatment. Raffinate phases are fed into the next evaporator. The pressures of evaporators (B105, B109, B113, B115) are set 0.384 atm, 0.298 atm, 0.289 atm and 0.211 atm. Vapor fractions are set as 0.6, 0.4, 0.3 and 0.1 [436]. The raffinate phase of the evaporators is fed in a flash distillation column (B120) with air. The gas phase is sent to wastewater and raffinate phase which includes solid unconverted sugars are sent to cogeneration part for combustion.

3.5.2.8 Wastewater treatment

The wastewater treatment process is designed for reducing organic and chemical particles in the wastewater. The wastewater treatment process includes the digestion part (blue box) which includes anaerobic and aerobic digestion and dehydration part (pink box). The simulation of the wastewater treatment process is shown in Figure 3.14. In the first part includes digestion reactors such as anaerobic digestion and aerobic digestion. The inlet streams of wastewater process are fed from acetic acid recovery (S69), distillation (S176) and cogeneration (S177) process. The inlet streams are mixed in a mixer (B126) and the temperature is cooled at 35°C by a heat exchanger (B127) for anaerobic digestion. The COD of wastewater stream should be calculated, and anaerobic digestion nutrients should be added to the reactor according to COD results. Anaerobic reactor (B129) is designed to reduce COD ratio to 10%. The reaction temperature is set 35°C and 1 atm. Table 3.12 and Table 3.13 show anaerobic reactions in gaseous phase and biomass production.

Table 3.12 : Gaseous production in the wastewater treatment process (anaerobic digestion).

Glucose → 3 CH_4 + 3 CO_2
Xylose → 2.5 CH_4 + 2.5 CO_2
Galactose → 3 CH_4 + 3 CO_2
Cellobiose + H_2O → 6 CH_4 + 6 CO_2
Mannose → 3 CH_4 + 3 CO_2
Glucooligomer + H_2O → 3CH_4 + 3CO_2
HMF + 3 H_2O → 3 CH_4 + 3 CO_2
Arabinose → 2.5 CH_4 + 2.5 CO_2
Xylitol → 2.75 CH_4 + 2.25 CO_2 + 0.5 H_2O
Extractives+0.88916 CH_4→0.3662 NH_3+ 0.00278H_2S+1.2811H_2O+1.88916CO_2
Furfural + 3 H_2O → 2.5 CH_4 + 2.5 CO_2
Lactic acid → 1.5 CH_4 + 1.5 CO_2
Acetic acid → CH_4 + CO_2
Glycerol → 1.75 CH_4 + 1.25 CO_2 + 0.5 H_2O
Succinic acid + 0.5 H_2O → 1.75 CH_4 + 2.25 CO_2
Xylooligomer + H_2O → 2.5 CH_4 + 2.5 CO_2
Mannooligomer + H_2O → 3 CH_4 + 3 CO_2
Galactooligomer + H_2O → 3 CH_4 + 3 CO_2
Soluble lignin + 5.875 H_2O → 6.4125 CH_4 + 3.5875 CO_2
4 Oil + 34 H_2O → 51 CH_4 + 21 CO_2
4 Levulinic acid + 6 H_2O → 11 CH_4 + 9 CO_2
4 Formic acid → CH_4 + 3 CO_2 + 2 H_2O
Cellulose + H_2O → 3 CO_2 + 3 CH_4
Xylan + H_2O → 2.5 CH_4 + 2.5 CO_2
Lignin + 5.875 H_2O → 6.4125 CH_4 + 3.5875 CO_2
Cellulase + 0.6735 H_2O → 0.50825 CH_4 + 0.49175 CO_2 + 0.29 NH_3 + 0.007 H_2S
Arabinan + H_2O → 2.5 CH_4 + 2.5 CO_2
Mannan + H_2O → 3 CH_4 + 3 CO_2
Galactan + H_2O → 3 CO_2 + 3 CH_4
ZYMO + 0.45 H_2O → 0.525 CH_4 + 0.475 CO_2 + 0.2 NH_3

Table 3.13 : Biomass production in the wastewater treatment process (anaerobic digestion).

Glucose → 7.75282 Biomass
Mannose → 7.75282 Biomass
Galactose → 7.75282 Biomass
Xylose → 6.46062 Biomass
Arabinose → 6.46062 Biomass
Xylitol → 6.54747 Biomass
Glucooligomer → 6.9776 Biomass
Galactooligomer → 6.9776 Biomass
Mannooligomer → 6.9776 Biomass
Ethanol → 1.98252 Biomass
Extractives → 4.2297 Biomass
Cellulose → 6.9775 Biomass
Xylan → 5.6854 Biomass
Lignin → 6.66312 Biomass
Cellulase → 0.95807 Biomass
ZYMO → 1.06386 Biomass
Xylooligomer → 5.68545 Biomass
Cellobiose→ 14.7305 Biomass
Furfural → 4.13492 Biomass
HMF → 5.42696 Biomass
Acetic acid → 2.58429 Biomass
Lactic acid → 3.87643 Biomass
Succinic acid → 5.08182 Biomass
Glycerol → 3.96318 Biomass
Oil → 12.1555 Biomass
Levulinic acid → 4.99626 Biomass
Formic acid → 1.98128 Biomass
Acetate → 2.58427 Biomass
Arabinan → 5.6854 Biomass
Mannan → 6.97754 Biomass
Galactan → 6.97754 Biomass
Ethanol → 1.5 CH_4 + 0.5 CO_2

After anaerobic digestion, the outlet stream is fed to flash distillation column (B130) to separate gas phase. Solid-liquid or also known as sludge phase is fed to the aerobic reactor (B132) with nutrients (S185) and air (S186) at 21.1°C and 1 atm. The aerobic digestion reactions are shown in Table 3.14 and Table 3.15. While Table 3.14 presents aerobic digestion reactions which produce biomass cell, Table 3.15 shows the aerobic reactions to produce the gaseous phase such as carbondioxide, water, and sulfurdioxide.

Table 3.14 : Biomass production in the wastewater treatment process (aerobic digestion).

Glucose → 7.75282 Biomass
Mannose → 7.75282 Biomass
Galactose → 7.75282 Biomass
Xylose → 6.46062 Biomass
Arabinose → 6.46062 Biomass
Xylitol → 6.54747 Biomass
Glucooligomer → 6.9776 Biomass
Galactooligomer → 6.9776 Biomass
Mannooligomer → 6.9776 Biomass
Xylooligomer → 5.68545 Biomass
Cellobiose → 14.7305 Biomass
Furfural → 4.13492 Biomass
HMF → 5.42696 Biomass
Ethanol → 1.98252 Biomass
Lactic acid → 3.87643 Biomass
Formic acid → 1.98128 Biomass
Extractives → 4.2297 Biomass
Levulinic acid → 4.99626 Biomass
Cellulose → 6.97754 Biomass
Xylan → 5.6854 Biomass
Lignin → 6.66312 Biomass
Cellulase → 0.958076 Biomass
ZYMO → 1.06386 Biomass
Acetate → 2.58427 Biomass
Arabinan → 5.6854 Biomass
Mannan → 6.97754 Biomass
Galactan → 6.97754 Biomass
Acetic acid → 2.58429 Biomass
Oil → 12.1555 Biomass
Succinic acid → 5.08182 Biomass
Glycerol → 3.96318 Biomass

Table 3.15 : Gaseous production in the wastewater treatment process (aerobic digestion).

Extractives → 1.1333 O_2 + 0.05487 H_2O + CO_2 + 0.3662 NO_2 + 0.00278 SO_2
Levulinic acid + 5.5 O_2 → 5 CO_2 + 4 H_2O
6 O_2 + Glucooligomer → 5 H_2O + 6 CO_2
12 O_2 + Cellobiose → 11 H_2O + 12 CO_2
6 O_2 + Glucose → 6 H_2O + 6 CO_2
6 O_2 + HMF → 3 H_2O + 6 CO_2
5 O_2 + Xylooligomer → 4 H_2O + 5 CO_2
5 O_2 + Xylose → 5 H_2O + 5 CO_2
5 O_2 + Furfural → 2 H_2O + 5 CO_2
6 O_2 + Mannooligomer → 5 H_2O + 6 CO_2
6 O_2 + Mannose → 6 H_2O + 6 CO_2
6 O_2 + Galactooligomer → 5 H_2O + 6 CO_2
6 O_2 + Galactose → 6 H_2O + 6 CO_2
2 Formic acid + O_2 → 2 H_2O + 2 CO_2
Cellulose + 6 O_2 → 5 H_2O + 6 CO_2
Xylan + 5 O_2 → 5 CO_2 + 4 H_2O
Lignin + 12.825 O_2 → 10 CO_2 + 6.95 H_2O
Cellulase + 1.2445 O_2 → 0.785 H_2O + CO_2 + 0.145 N_2 + 0.007 SO_2
ZYMO + 1.2 O_2 → CO_2 + 0.9 H_2O + 0.1 N_2
Acetate + 2 O_2 → 2 CO_2 + 2 H_2O
Arabinan + 5 O_2 → 5 CO_2 + 4 H_2O
Mannan + 6 O_2 → 6 CO_2 + 5 H_2O
Galactan + 6 O_2 → 6 CO_2 + 5 H_2O

The outlet stream of the aerobic reactor (S187) is fed to flash distillation column to separate gas and liquid-solid phase. Gas phase (S188) is mixed with anaerobic digestion gases in a mixer (B131) and sent to cogeneration process for combustion. The sludge phase (S190) is sent to a solid-liquid separator to reduce the water ratio of sludge. Three solid-liquid separators (B134, B135, and B136) are designed in this process, and the sludge/water ratios are set as 5% for the first drier (B134), 10% for the second drier (B135), and 25% for the third drier (B136). Then, sludge is sent to drier to increase sludge/water ratio is 95%. The drier (B138) is designed as contact drier with 8 meters length. The exit of the B138 drier, sludge stream consist of 5% of moisture. This ratio is enough for to send sludge for combustion. The streams that separate in driers in liquid phase are collected and formed as process waste water. It is numbered as S202. COD calculations were done and showd in results. Finally, the sludge stream (S200) is sent to the cogeneration for combustion and produce heat and electricity.

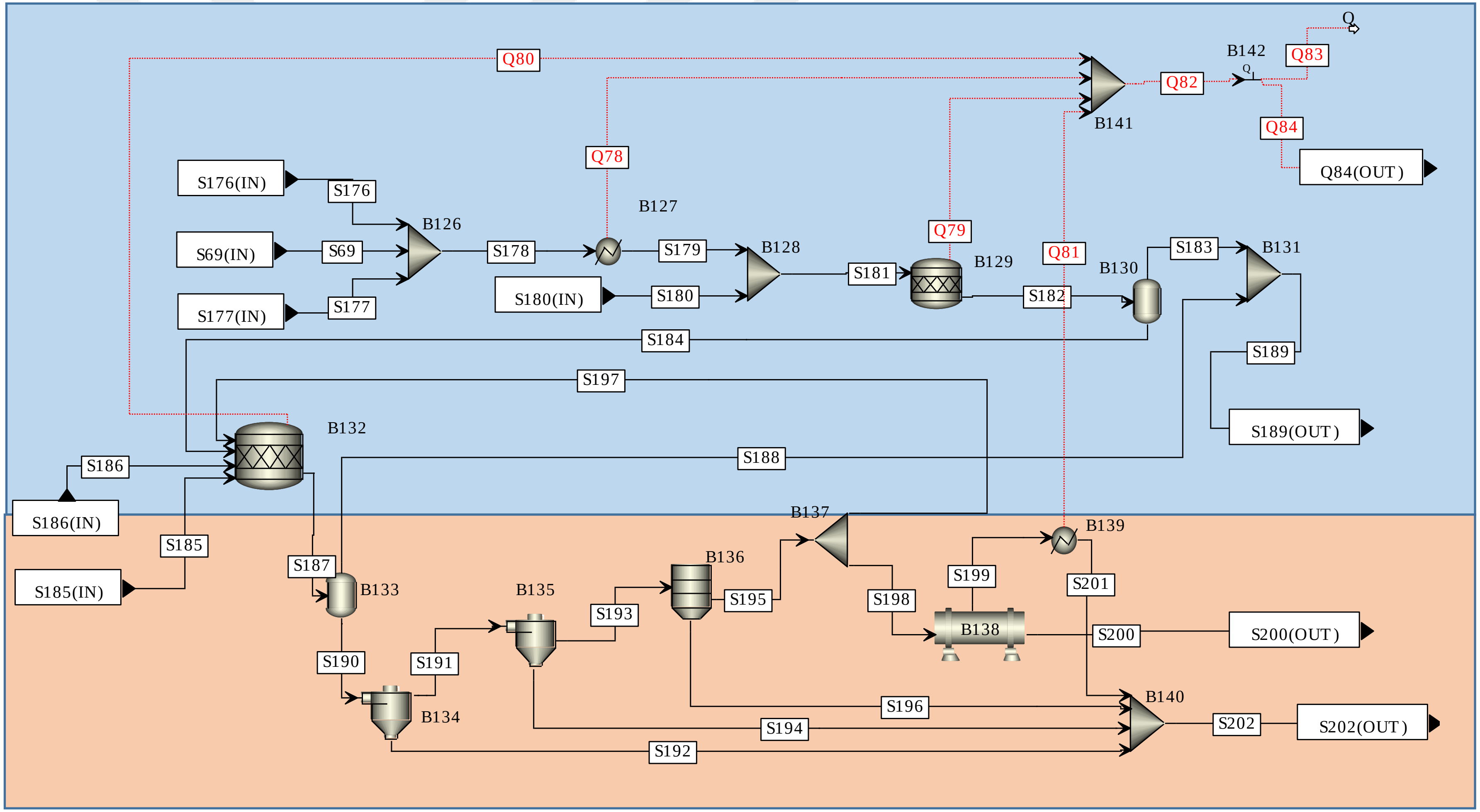


Figure 3.14 : Wastewater treatment process flowsheet in Aspen Plus process simulation software.

The heat streams (Q78, Q79, Q80, and Q81) which produced by unit operation blocks (B127, B129, B132, and B139) are mixed in a heat mixer (B141). The total heat production is excess heat for wastewater treatment. Then, 10% of total heat (Q83) is assumed to be lost in the process, and rest of heat (Q84) is sent to the utilities unit for using other processes.

3.5.2.9 Cogeneration

The cogeneration process is designed to produce bioheat and biopower from solid wastes of IOBB. This process contains two main parts. The first one is the combustion part (blue box) which is material streams from combustion to waste (gas and liquid forms), and the other (pink box) is the steam cycle which used heat duty from combustion and produced bioheat and biopower. The design of the process of cogeneration is shown in Figure 3.15 below. In the cogeneration part, first of all, the streams from wastewater treatment process (S189 and S200), from organosolv pretreatment process (S12), distillation process (S171) and acetic acid recovery process (S77) are mixed in a mixer (B143) and fed in the combustion reactor (B144). The combustion reactor operates at 950°C and 1 bar. For air requirement, 40% of excess air is firstly feed in the heat exchanger (B149). The heat exchanger is modeled as a shortcut heat exchanger, and shortcut flow direction is defined as multipass. The hot stream outlet temperature is set at 219°C. Then, hot air is fed to the combustion reactor. The stoichiometry of combustion reactions is shown in Table 3.16.

On the other hand, barks (S205) from the SOC is fed another combustion reactor with hot air (S206). The combustion reactor operates at 950°C and 1 bar. The outlet hot gas stream from the combustion reactors (S204 and S208) is fed in a solid separator (B147) to separate ash from the gas stream. The hot gas is cooled in heat exchanger (B148) and then sent to another heat exchanger for cold heating air. The cold air is heated in a heat exchanger (B149). B149 is a “HeatX” shortcut model and designed as multipass, con-current flow direction. In B149, while the cold air is heated, stack gas is cooled before the emitting the atmosphere. At B150, the stack gas is cooled at the room temperatures and separates exhaust gases from other components in flash distillation (B151). Liquid bottom stream (S177) is fed into the wastewater treatment process and gas phase (S217) is sent to the gas collector.

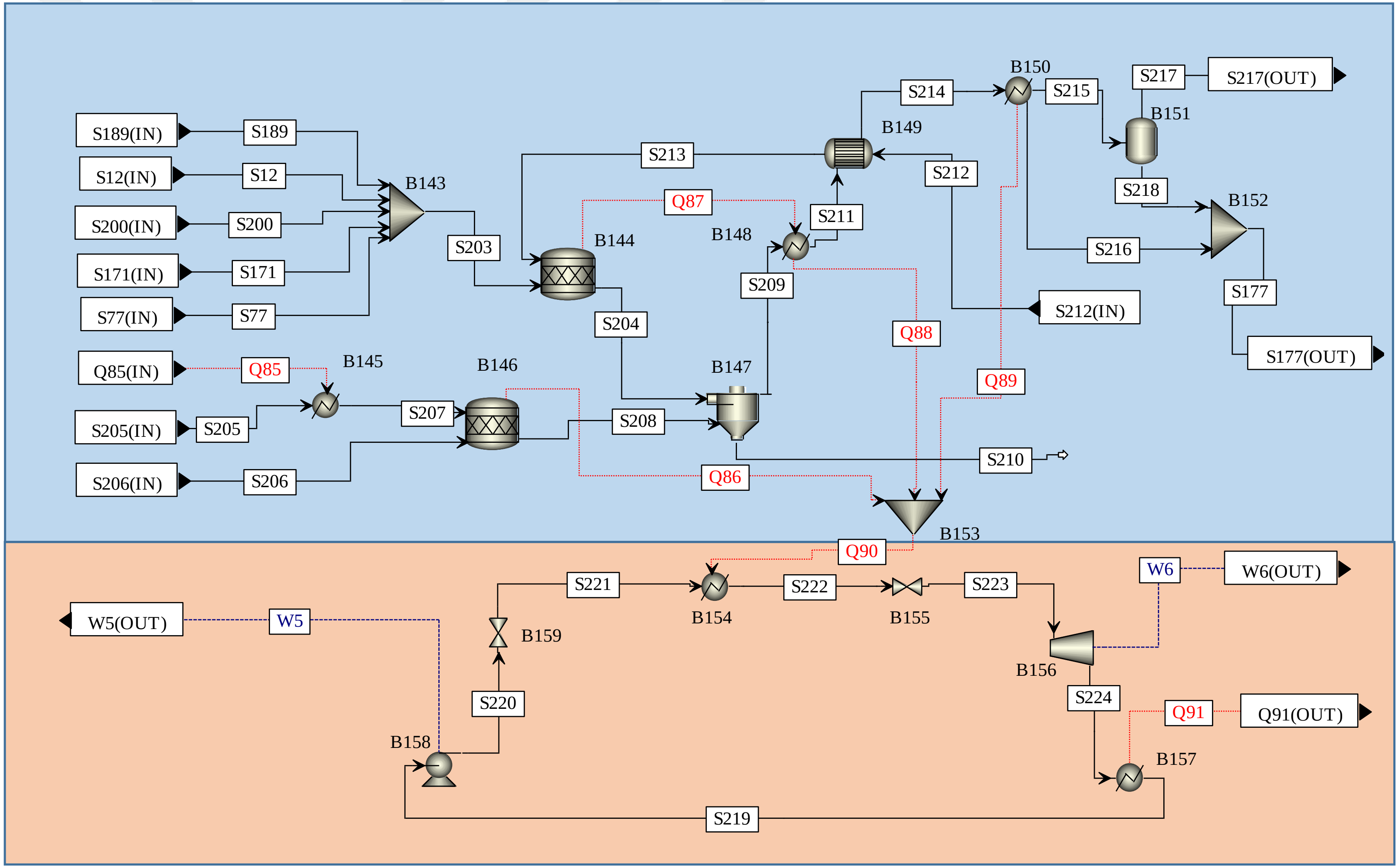


Figure 3.15 : Cogeneration process flowsheet in Aspen Plus simulation software.

Table 3.16 : The reaction stoichiometry of combustion.

CH_4 + 2 O_2 → CO_2 + 2 H_2O
Cellulose + 6 O_2 → 5 H_2O + 6 CO_2
Xylan + 5 O_2 → 5 CO_2 + 4 H_2O
Arabinan + 5 O_2 → 5 CO_2 + 4 H_2O
Mannan + 6 O_2 → 5 H_2O + 6 CO_2
Lignin + 12.825 O_2 → 6.95 H_2O + 10 CO_2
Acetate + 2 O_2 → 2 CO_2 + 2 H_2O
Galactan + 6 O_2 → 5 H_2O + 6 CO_2
Glucooligomer + 6 O_2 → 5 H_2O + 6 CO_2
Cellobiose + 12 O_2 → 12 CO_2 + 11 H_2O
Glucose + 6 O_2 → 6 CO_2 + 6 H_2O
HMF + 6 O_2 → 3 H_2O + 6 CO_2
Xylooligomer + 5 O_2 → 4 H_2O + 5 CO_2
Xylose + 5 O_2 → 5 H_2O + 5 CO_2
Furfural + 5 O_2 → 2 H_2O + 5 CO_2
Tar + 5 O_2 → 5 H_2O + 5 CO_2
Mannooligomer + 6 O_2 → 5 H_2O + 6 CO_2
Mannose + 6 O_2 → 6 H_2O + 6 CO_2
Galactooligomer + 6 O_2 → 5 H_2O + 6 CO_2
Galactose + 6 O_2 → 6 H_2O + 6 CO_2
Arabooligomer + 5 O_2 → 4 H_2O + 5 CO_2
Arabinose + 5 O_2 → 5 H_2O + 5 CO_2
Acetooligomer + 2 O_2 → 2 H_2O + 2 CO_2
Acetic acid + 2 O_2 → 2 H_2O + 2 CO_2
Lactic acid + 3 O_2 → 3 H_2O + 3 CO_2
Cellulase + 1.2445 O_2 → 0.785 H_2O + CO_2 + 0.145 N_2 + 0.007 SO_2
Ethanol + 3 O_2 → 3 H_2O + 2 CO_2
ZYMO + 1.2 O_2 → 0.9 H_2O + CO_2 + 0.1 N_2
Glycerol + 3.5 O_2 → 4 H_2O + 3 CO_2
Succinic acid + 3.5 O_2 → 3 H_2O + 4 CO_2
Xylitol + 5.5 O_2 → 6 H_2O + 5 CO_2
Biomass + 1.2185 O_2 → 0.82 H_2O + CO_2 + 0.115 N_2 + 0.0035 SO_2
SO_2 + 0.5 O_2 + H_2O → H_2SO_4
H_2S + 1.5 O_2 → SO_2 + H_2O
0.5 N_2 + O_2 → NO_2
H_2SO_4 → SO_2 + H_2O + 0.5 O_2
Oil + 25.5 O_2 → 18 CO_2 + 17 H_2O
Extractives → 1.4995 O_2 + 0.05487 H_2O + CO_2 + 0.18312 N_2 + 0.00278 SO_2
CO_2 → CO + 0.5 O_2
Soluble lignin + 12.825 O_2 → 6.95 H_2O + 10 CO_2
Levulinic acid + 5.5 O_2 → 5 CO_2 + 4 H_2O
Formic acid + 0.5 O_2 → CO_2 + H_2O
CSL + 6 O_2 → 6 H_2O + 6 CO_2

The two heat exchanger (B148 from combustion side and B154 from steam turbine side) is connected to transfer heat duty of combustion to the steam generator to provide to the connection between combustion part and steam cycle part [60]. At the steam cycle side, two heat exchangers (B154 and B157), one turbine (B156) and one pump (B158) are installed to complete the steam cycle. The inlet steam stream of the turbine is 301°C and 42 atm. Turbine discharge pressure is set 12 atm and type is isentropic. “W6” stream indicates the outlet work stream of the turbine and it is defined to gained power during cogeneration. The other heater (B157) is cooled the stream and gained “Q91” from the cogeneration. Then the pump increased the pressure again at 42 atm and heated at heat exchanger (B154) again. Thus, the steam cycle is completed.

3.5.2.10 Exhaust gas collection

Gas mixtures are collected in a collector before emitting to air from enzyme production (S106), distillation (S165) and cogeneration (S217) process. Three gas streams are fed in a mixer (B178), and total gas production from the whole biorefinery is defined (S229). It has to be controlled to be in legal limits. The design of the exhaust gas is given in Figure 3.16.

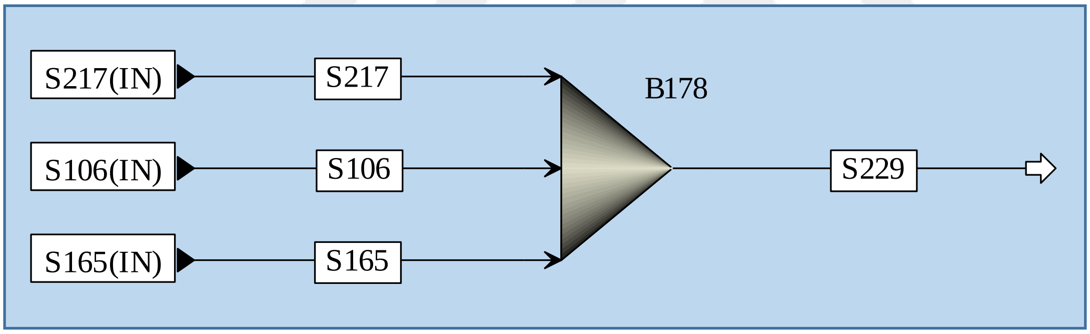


Figure 3.16 : Exhaust gas collection flowsheet in Aspen Plus simulation software.

3.5.2.11 Storage

Storage is the section in which all products are stored as long as they sell. In this simulation four products exist. These are bioethanol, organosolv lignin, furfural, and acetic acid. Thus, four storage tanks are located in the storage part. STORETOH, STORLGNN, STORFURF, and STORACAD are for bioethanol, organosolv lignin, furfural, and acetic acid.

3.5.2.12 Utilities

Utilities are designed to serve requirements of heat and power for each process. B160 mixer is mixed the excess heat streams from the processes, and B161 heat splitter is divided heat streams for requirements of processes. Q26 is sent to the furfural production process, while Q43 is sent to enzyme production and Q85 is sent to cogeneration process. Q93 is the excess heat and should be defined as a valuable product.

B162 mixer collects all work streams, and work splitter (B163) divides the stream for process requirement (W8) and feed into the grid (W9). The design of the utilities section is shown in Figure 3.17.

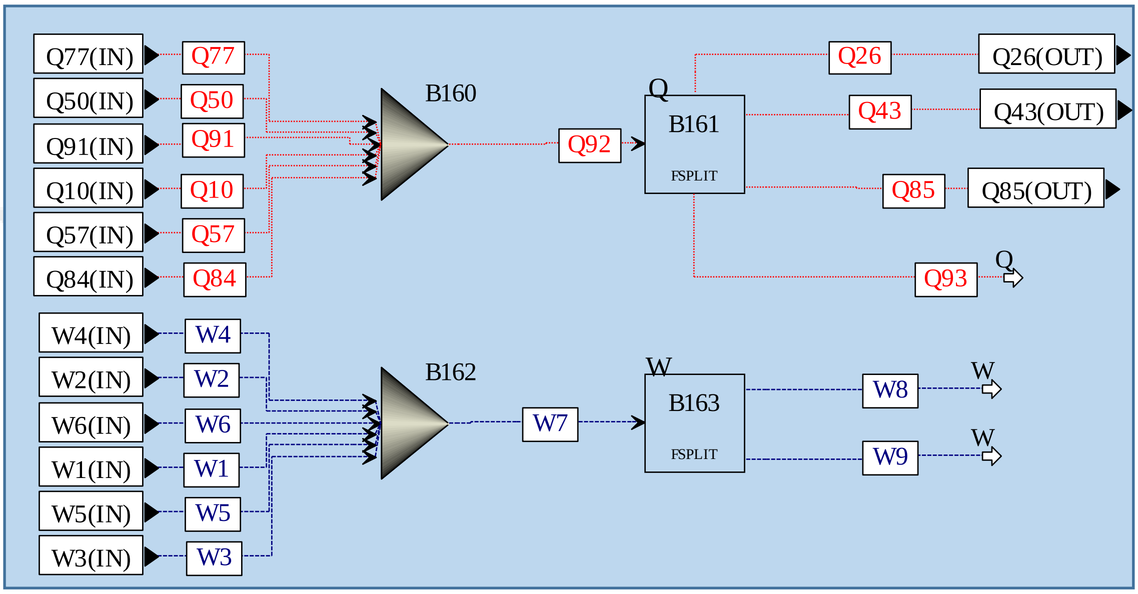


Figure 3.17 : Utilities flowsheet in Aspen Plus simulation software.

3.5.3 Design specifications

Design specifications are used to obtain the desired components properties. Notably, in distillation columns, desired product purity is set, and range of one other variable such as reflux rate, distillate to raffinate ratio, distillate flow rate or raffinate flow rate is determined. After the calculation, Aspen Plus simulation software gives the exact variable result to obtain the desired purity of the product. For example, to obtain 99.5% purity of bioethanol, the bottom rate is selected as 100 to 1000 kg/h. Aspen Plus simulation program calculates the distillation column and indicates that for 99.5% purity of bioethanol, the bottom rate must be 459 kg/h. This tool is allowed to obtain the desired product easily. In distillation columns, design specifications are used in the simulation.

3.5.4 Calculator blocks

Calculator blocks are used for altering streams according to other streams results. Fortran statements are required for the calculation. There are 22 calculation blocks are applied in the IOBB simulation. Calculator blocks provide accuracy for altering or modifying stream. Table 3.17 presents the calculator blocks and application areas.

Table 3.17 : Calculator blocks and their effected streams.

Calculator Name	Affected Stream	Application
CAL1	S3	Catalyst requirement for B1
CAL2	S19	Water requirement for B10
CAL3	S23	Water requirement for B14
CAL4	S28	Water requirement for B17
CAL5	S47	H_2SO_4 requirement for B31
CAL6	S62	Make-up undecane requirement for B44
CAL7	S86	Ammonia requirement for B60
CAL8	S87	CSL requirement for B60
CAL9	S88	Air requirement for B60
CAL10	S96	Ammonia requirement for B66
CAL11	S97	Nutrients requirement for B66
CAL12	S98	CSL requirement for B66
CAL13	S100	Oil requirement for B66
CAL14	S115	CSL requirement for B86 & B87
CAL15	S116	DAP requirement for B86 & B87
CAL16	S119	CSL requirement for B82
CAL17	S120	DAP requirement for B82
CAL18	S160	Air requirement for B120
CAL19	S180	Nutrients requirement for B129
CAL20	S185	Nutrients requirement for B132
CAL21	S206	Air requirement for B146
CAL22	S212	Air requirement for B144

Especially for chemical requirements, using calculator blocks are efficiency. For example, CAL21 is calculated air requirement for combustion in B146 block. When the inlet streams of B146 are changed, the required air stream is calculated by CAL21 and modify to the S206 air stream. Thus, individually control, and changes are preventing by calculator blocks. Additionally, the possibility of human errors is reduced.

3.5.5 Validation of Aspen Plus process simulation model

For validation of the Aspen Plus process simulation, each process is designed individually, and the results are compared with the reference studies. Organosolv pretreatment and acetic acid recovery processes are based on the study which was published by Kautto et al. (2013) with the title “Design and simulation of an organosolv process for bioethanol production” [265, 285],

Validation of furfural production process three studies are taken as reference in this study. First of all, furfural production part is based on the study which published by Morales et al. (2010) with the title “Simulation of Furfural Production Process for Revamping with Ethanol Technology from Lignocellulosic Residuals” and “Hemicellulose Biorefinery for Furfural Production: Energy Requirement Analysis and Minimization” published by Montastruc et al. (2011). Also, the study published by Kautto et al. (2013) is taken as reference in furfural recovery part [50, 285, 297].

NREL Report (TP-510-32438) which is titled as “Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover” was chosen as a reference for enzyme production, saccharification and fermentation, distillation and wastewater treatment processes [436]. For cogeneration part, two reference studies are used. The combustion side is compared with NREL report and the study which is title as “LCA of Combined Bioheat and Biopower Production and Cost: Simulated Case Studies Based on Combustion Utilizing Turkish Oak (Quercus Cerris L.) Coppices” was chosen as a reference for the cogeneration process Rankine cycle part [60].

The unit operation blocks, parameters, and specifications have selected the references above. However, some unit operation block parameters vary depending on inlet streams. In these situations, calculations were done and parameters selected according to calculation results.

3.5.5.1 Organosolv pretreatment part

For organosolv pretreatment validation, components of inlet streams (biomass, solvent, and catalyst) were chosen following the study of [265]. At their study, reaction kinetics or yield was not defined. Thus, kinetics and yields were assumed to depend on their inlet and outlet stream components. Also, unit operation blocks were designed as the work of Kautto et al. (2013) [285]. Table 3.18 shows the structural analysis of feedstock which used in validation of Aspen Plus organosolv pretreatment and the literature and Aspen Plus simulation data.

Table 3.18 : Structural analysis of hybrid poplar [265].

Component	Mass Fraction (%)
Klason Lignin	21
Acid Soluble Lignin	2.3
Glucan	44.1
Xylan	15.7
Mannan	3.5
Galactan	0.3
Arabinan	4.5
Ash	1.4
Extractives	2.5
Acetyl Groups	3.3
Other	1.4

According to Table 3.18, feedstock definition were defined as above. These datas are input in the Aspen Plus simulation programme and results of Aspen Plus simulation programme and literature datas were compared. In Table 3.19, while O_{out} indicates organosolv reactor output stream, PH_{out} indicates post-hydrolysis reactor output streams.

Table 3.19 : Literature data and Aspen Plus simulation software results for soluble fractions.

	Literature Data (MT/h)		Aspen Plus (MT/h)		Consistency (%)	
Components	O_{out}	PH_{out}	O_{out}	PH_{out}	O_{out}	PH_{out}
Glucose	0.2	0.5	0.22	0.661	90.00	67.80
Xylose	3.9	9	3.892	9.301	99.80	96.66
HMF	0.2	0.1	0.204	0.133	98.00	67.00
Arabinose	3.7	3.7	3.671	3.671	99.22	99.22
Galactose	0.1	0.3	0.11	0.328	90.00	90.67
Mannose	0.4	1.2	0.441	1.322	89.75	89.83
Glucooligomer	0.4		0.397		99.25	
Xylooligomer	4.8		4.76		99.17	
Tar	1.3	1.3	1.219	1.321	93.77	98.38
Mannooligomer	0.8		0.793		99.13	
Galactooligomer	0.2		0.196		98.00	
Acetooligomer	1.5		1.487		99.13	
Extractives	2.5	2.5	2.917	2.917	83.32	83.32
Soluble Ash	0.9	0.9	0.916	0.916	98.22	98.22
Furfural	2.4	2.7	2.4	2.4	100.00	88.89
Acetic acid	1.2	2.7	1.19	2.677	99.17	99.15
Levulinic acid	2.6	2.6	2.53	2.53	97.31	97.31
Formic acid	1	1	1.003	1.003	99.70	99.70

Table 3.20 : Literature data and Aspen Plus simulation software results for solid fraction results.

Components	Literature Data (MT/h)		Aspen Plus (MT/h)		Consistency (%)	
	Lignin	Pulp	Lignin	Pulp	Lignin	Pulp
Cellulose		38.8		40.248		96.27
Xylan		3		3.01		99.67
Lignin	15.5	5.9	15.713	5.851	98.63	99.17
Unknown		1.4		1.388		99.14
Acetate		0.6		0.595		99.17
Arabinan		0.8		1.232		46
Mannan		1.3		1.371		94.54
Galactan		0		0.002		
Ash		0.6		0.472		78.67

Published articles defined that 90% of consistency is acceptable for simulation [285]. In this simulation, minimum consistency was found at 91.5%. Besides, at the most critical components such as cellulose, glucose, xylose, lignin, acetic acid and furfural, consistencies were found a minimum of 95%.

3.5.5.2 Furfural production

In the literature, several studies about designing of furfural production are found. However, only experimental studies for furfural production with H_2SO_4 catalyst found in the literature. In the furfural production process, xylose to furfural conversion rate is found that 75% of xylose is converted to furfural [50, 297]. Furfural production reaction occurs only in one reactor, and Aspen Plus allows to select reaction yield. Therefore, in IOBB simulation, furfural yield is taken directly 75%. Furfural recovery part is referred from Kautto et al. [285]. Comparison of literature data and Aspen Plus simulation software is presented in Table 3.21.

Table 3.21 : Literature data and Aspen Plus simulation results for furfural recovery.

	Literature Data (MT/h)		Aspen Plus (MT/h)		Consistency (%)	
Components	Solvent Recovery	Furfural	Solvent Recovery	Furfural	Solvent Recovery	Furfural
Ethanol	0.04	0.00	0.0398	2.0E-04	99.50	99.98
Water	0.06	0	0.0595	0.0005	99.17	99.99
Furfural	0.01	0.44	0.011	0.43	90.91	97.67
Acetic acid	0.01	0	0.01	0	100.00	100.00

3.5.5.3 Acetic acid recovery

The acetic acid recovery process is designed to base on the study which was published by Kautto et al. [285]. Operation temperatures, pressures, and other parameters are referred from their study. Table 3.22 compares the reference study and Aspen Plus simulation software results.

Table 3.22 : Literature data and Aspen Plus simulation software results for acetic acid recovery.

Components	Literature Data (MT/h)			Aspen Plus (MT/h)			Consistency (%)		
	R	MA	AA	R	MA	AA	R	MA	AA
Water	251.01	0.18		250.97	0.22		99.98	77.78	
Furfural	0.01		0.02	0.012		0.018	80.00		90.00
Acetic Acid	0.13	0.29	1.26	0.134	0.294	1.263	96.92	98.62	99.76
Formic Acid	0.01	0.46		0.011	0.459		90.00	99.78	
Levulinic Acid	0.01		0.02	0.011		0.019	90.00		95.00

In Table 3.22, “R” indicated raffinate phase, while “D” is the distillate phase, “MA” is mixed acids and “AA” is acetic acid. It is seen that acetic acid recovery process results which calculate by Aspen Plus simulation software are consistent with reference study. Therefore, this design is assumed as acceptable.

3.5.5.4 Enzyme production

For validation of enzyme production process, NREL Report is chosen as a reference study. Also, reaction yields, nutrient ratios and operation parameters are set according to the NREL Report. The main outlet streams of NREL Report and Aspen Plus simulation software are presented in Table 3.23.

According to Table 3.23, the consistency between NREL Report and Aspen Plus simulation software is high enough. Therefore, this design can be applied in the organosolv based biorefinery simulation.

3.5.5.5 Saccharification and fermentation

Bioethanol production flowsheet was designed according to NREL Report inlet stream, equipment choice and operation parameters. In this flowsheet is occurred one main inlet stream and two outlet streams. Inlet stream was obtained from the outlet stream of the pretreatment section. In the NREL Report and Aspen Plus simulation,

Table 3.23 : Literature data and Aspen Plus simulation software results for enzyme production.

	NREL report (kg/h)		Aspen Plus (kg/h)		Consistency (%)	
Components	Gas	Liquid	Gas	Liquid	Gas	Liquid
Soluble lignin	9.83E-28	4.23E-05	9.32E-28	4.11E-05	94.89	97.16
HMF	4.74E-10	6.39E-06	4.68E-10	6.19E-06	98.69	96.87
Glucooligomers	9.55E-28	4.01E-05	9.48E-28	4.01E-05	99.25	99.95
Cellobiose	3.30E-28	1.42E-05	3.30E-28	1.42E-05	99.93	100.00
Xylooligomers	2.52E-20	2.47E-05	2.51E-20	2.31E-05	99.69	93.53
Mannooligomers	4.26E-29	1.83E-06	4.24E-29	1.83E-06	99.53	99.67
Galactooligomers	5.30E-29	2.28E-06	5.22E-29	2.12E-06	98.45	92.98
Arabooligomers	3.49E-21	3.43E-06	3.48E-21	3.17E-06	99.69	92.42
Xylitol	4.87E-28	2.02E-05	4.86E-28	2.00E-05	99.87	99.06
Extractives	5.11E-27	0.00022	5.09E-27	0.00021	99.65	97.77
Ethanol	1.12E-06	3.96E-07	1.10E-06	3.54E-07	98.21	89.39
H_2O	0.002948016	0.01827	0.002948016	0.01657	100.00	90.70
Furfural	2.28E-05	1.46E-05	2.25E-05	1.46E-05	98.68	100.00
H_2SO_4	3.12E-12	6.64E-06	2.84E-12	6.41E-06	91.02	96.54
N_2	0.1563258	4.40E-07	0.1563258	4.25E-07	100.00	96.59
CO_2	0.001839197	2.63E-07	0.001835197	2.48E-07	99.78	94.29
O_2	0.04023912	2.19E-07	0.04023912	2.17E-07	100.00	99.13
Lactic acid	1.16E-09	3.93E-05	1.15E-09	3.93E-05	99.00	100.00
Acetic acid	1.99E-05	0.00019	1.99E-05	0.00019	99.94	100.00
Glycerol	3.89E-12	4.78E-06	3.84E-12	4.66E-06	98.64	97.49
Succinic acid	2.58E-12	1.36E-05	2.52E-12	1.34E-05	97.71	98.53
Oil	7.44E-13	0.00014	7.42E-13	0.00014	99.65	98.91
CSL	5.57E-27	0.00024	5.51E-27	0.00023	98.85	99.03
CNUTR	1.98E-27	9.41E-05	1.92E-27	9.21E-05	96.87	97.87
Xylan		1.42E-05		1.42E-05		100.00
Lignin		0.00046		0.00046		100.00
Cellulase		0.00033		0.00033		100.00
Biomass		0.00015		0.00015		100.00
ZYMO		1.11E-05		1.10E-05		99.10
Arabinan		1.97E-06		1.97E-06		99.85
Tar		8.15E-06		8.11E-06		99.51
Ash		0.00014		0.00014		100.00

the content of the inlet stream was the defined same and was showed in the second column in Table 3.24.Outlet streams were obtained in the liquid phase and the gas phase. The liquid phase mainly consists of ethanol and water, and this stream has to be dehydrated. Thus, it is named is Undehydrated Bioethanol Stream. The comparison of the NREL Report and Aspen Plus simulation outputs are shown in Table 3.24. Gas phase contains mainly CO_2 which occurs from fermentation, and this stream is named as Gaseous By-Products Stream. Also, the comparison of the NREL Report and Aspen Plus simulation outputs for gaseous by-products stream are shown in Table 3.25.

In Table 3.25 “SF” is indicated seed fermentor and “F” is indicated fermentor. According to Table 3.24 and Table 3.25, at bioethanol production part, the consistency between NREL Report outputs and Aspen Plus simulation software outputs is high. It is clearly stated that this simulation flowsheet is applicable for IOBB simulation.

Table 3.24 : Literature data and Aspen Plus simulation software results for undehydrated bioethanol stream.

Components	Inlet Stream (kg/h)	NREL Report Outputs (kg/h)	Aspen Plus Outputs (kg/h)	Consistency (%)
Glucose	2432.525	81.9940	81.9940	100
Cellulose	28432.18	1364.7450	1364.7450	100
Xylose	18089.18	908.7370	906.0370	99.70
Xylan	439.259	439.2590	439.2590	100
Lignin	14251.83	14251.8280	14251.8310	100
Cellulase	81.202	649.6190	649.6190	100
ZYMO	136.026	1088.2110	1087.4730	99.93
Soluble Solids	1205.612	1205.6120	1205.6120	100
Arabinose	2527.828	217.0560	217.0560	100
Galactose	1642.127	141.0040	141.0040	100
Mannose	1320.473	113.3840	113.3840	100
Arabinan	60.875	60.8750	60.8750	100
Mannan	32.522	32.5220	32.5220	100
Galactan	40.444	40.4440	40.4440	100
Extractives	5037.734	5037.7350	5037.7340	100
Ash	4361.315	4361.3150	4361.3150	100
Ethanol	32.146	24812.0160	25161.2000	98.59
Water	335254.8	374108.5320	374262.4050	99.96
Furfural	642.387	642.5890	649.2470	98.96
H_2SO_4	152.332	152.3320	152.3320	100
CO_2		451.4110	451.3160	99.98
O_2	0.165	0.1780	0.1780	100
Levulinic Acid	482.401	2078.3170	2076.7570	99.92
Acetic Acid	4528.708	5309.7770	5310.3270	99.99
DAP		147.4520	147.4640	99.99
CSL		1249.0380	1249.0800	100

Table 3.25 : Literature data and Aspen Plus simulation software results for the gas stream.

Components	NREL Report Outputs (kg/h)		Aspen Plus Simulation Outputs (kg/h)		Consistency (%)	
	SF	F	SF	F	SF	F
Ethanol	69.846	666.162	70.2520	665.0690	99.42	99.84
H_2O	76.19	709.293	76.5910	708.5940	99.47	99.90
Furfural	0.803	7.403	0.8060	7.3950	99.63	99.89
N_2	0.034	0.303	0.0340	0.3030	100	100
CO_2	2230.603	20763.094	2230.8520	20743.473	99.99	99.91
O_2	20.018	176.218	20.0180	175.8930	100.0	99.82
Levulinic Acid	< 0.001	0.001	< 0.001	0.0010		100
Acetic Acid	0.678	6.279	0.6800	6.2730	99.71	99.90

3.5.5.6 Distillation

The distillation process is one of the most complex processes because of containing azeotropic components. For validation of the distillation process, the NREL report is taking as a resource, and the consistency was calculated [436]. The inlet stream of the NREL report is shown in Table 3.26.

Table 3.26 : Distillation part inlet streams.

Components	Gas 1 (kg/h)	Gas 2 (kg/h)	Sugar Solution (kg/h)	Water (kg/h)	Air (kg/h)
Glucose	trace	trace	81.993		
Cellulose			1364.747		
Xylose	trace	trace	908.709		
Xylan			439.259		
Lignin			14251.85		
Cellulase			649.62		
ZYMO			1088.213		
Soluble Solids	trace	trace	1204.691		
Gypsum			28.464		
Soluble Lignin	trace	trace	968.155		
HMF	< 0.001	< 0.001	146.342		
Arabinose	trace	trace	217.044		
Galactose	trace	trace	140.996		
Mannose	trace	trace	113.378		
Arabinan			60.875		
Mannan			32.522		
Galactan			40.444		
Tar			251.485		
Arabolig	trace	trace	78.572		
Xylitol	trace	trace	1073.426		
Extractives	trace	trace	5033.887		
Protein	trace	trace	3334.412		
Ash			4361.321		
Ethanol	69.846	666.161	24811.533		
H_2O	76.19	709.292	374082.597	35747	
Furfural	0.803	7.403	642.578		
H_2SO_4	trace	trace	152.285		
N_2	0.034	0.303	< 0.001		4677.528
CO_2	2230.601	20763.044	451.374		
O_2	20.018	176.218	0.178		1243.393
Levulinic Acid	< 0.001	0.001	2076.69		
Acetic Acid	0.678	6.279	5305.537		
Glycerol	trace	trace	253.695		
Succinic Acid	trace	trace	720.343		
DAP	trace	trace	147.432		
CSL	trace	trace	1248.875		

According to Table 3.26 inlet data, NREL report and Aspen Plus simulation results are compared and presented in Table 3.27 and Table 3.28.

Table 3.27 : Literature data and Aspen Plus simulation software results for outlet streams of gas scrubber column.

Components	NREL Report (kg/h)		Aspen Plus simulation (kg/h)		Consistency (%)	
	Distillate	Raffinate	Distillate	Raffinate	Distillate	Raffinate
HMF	3.63E-24	0.0001724	3.33E-24	0.0001723	91.94	99.99
Ethanol	4.317244	792.7736	4.00022	764.833	92.65	96.47
H_2O	432.6292	36120.01	430.1394	36112.57	99.42	99.97
Furfural	0.008783	8.407915	0.008359	8.289879	95.17	98.59
H_2SO_4	3.94E-35	1.94E-06	3.55E-35	1.94E-06	90.11	99.99
N_2	0.336915	1.15E-05	0.336914	1.15E-05	99.99	99.93
CO_2	23381.26	34.06329	23392.31	34.25131	99.95	99.44
O_2	196.4016	0.0126403	196.4013	0.0126559	99.99	99.87
Levulinic Acid	4.44E-25	0.001530	3.99E-25	0.0015299	89.96	99.98
Acetic Acid	8.17E-08	7.011719	7.75E-08	6.982873	94.79	99.58
Glycerol	8.98E-34	5.73E-06	8.10E-34	5.73E-06	90.16	99.99
Succinic Acid	1.80E-36	3.67E-06	1.62E-36	3.67E-06	89.98	99.99

Table 3.28 : Literature data and Aspen Plus simulation software results for outlet streams of the distillation process.

Components	NREL Report (kg/h)		Aspen Plus (kg/h)		Consistency (%)	
	Ethanol	to Combust	Ethanol	to Combust	Ethanol	to Combust
Glucose		63.10		61.545		97.54
Xylose		699.28		686.25		98.14
Arabinose		167.03		163.209		97.71
Galactose		108.50		107.273		98.87
Mannose		87.25		86.068		98.65
Ethanol	24568.79	2.70	24605.58	2.824	99.85	95.40
H_2O	123.014	43999.6	120.968	43247.32	98.34	98.29
Furfural	0.005	10.04	0.00475	10.679	95	93.61
H_2SO_4		117.21		115.008		98.12
Lactic acid		1590.30		1569.715		98.71
Acetic acid		2154.05	0.021	2051.235		95.22
Succinic acid		554.72		538.242		97.03
DAP		147.45		145.432		98.63
CSL		1249.04		1248.875		99.99
Cellulose		1357.92		1357.923		99.99
Xylan		437.06		442.063		98.86
Lignin		14180.5		14262.59		99.42
Cellulase		568.42		568.417		99.99
ZYMO		952.19		952.186		99.99
Arabinan		60.57		62.591		96.66
Mannan		32.36		32.36		100
Galactan		40.24		40.242		100

NREL report and Aspen Plus simulation software results have high consistency. Therefore, this distillation process simulation is assumed to be applicable.

3.5.5.7 Wastewater treatment

For validation of the wastewater treatment process, the anaerobic and aerobic digestion parameters are designed according to NREL report [436, 437]. Table 3.29 and Table 3.30 indicates the NREL Report and Aspen Plus simulation software and consistency for results of anaerobic digester outlet, aerobic digester outlet, and process water.

Table 3.29 : Literature data and Aspen Plus simulation software results for wastewater treatment.

Components	NREL Report (kg/h)				Aspen Plus simulation (kg/h)		
	Anaerobic inlet	Anaerobic outlet	Aerobic outlet	Water	Anaerobic outlet	Aerobic outlet	Water
Glucose	5.49E-16	3.84E-17	0	0	3.81E-17	0	0
Soluble lignin	2.01E-16	1.41E-17	0	0	1.40E-17	0	0
HMF	0.001670	0.000116	1.17E-5	1.16E-5	0.000116	1.17E-5	1.06E-5
Arabinose	2.62E-10	1.83E-11	0	0	1.83E-11	0	0
Galactose	3.66E-16	2.56E-17	0	0	2.54E-17	0	0
Mannose	2.95E-16	2.06E-17	0	0	2.03E-17	0	0
G.oligomers	6.16E-17	4.32E-18	0	0	4.31E-18	0	0
Cellobiose	2.81E-17	1.97E-18	0	0	1.96E-18	0	0
X.oligomers	5.52E-11	3.86E-12	0	0	3.86E-12	0	0
Mannoolig.	8.33E-18	5.83E-19	0	0	5.82E-19	0	0
Galactoolig.	1.04E-17	7.26E-19	0	0	7.21E-19	0	0
Araboolig.	7.64E-12	5.35E-13	0	0	5.35E-13	0	0
Xylitol	4.40E-18	3.08E-19	0	0	3.08E-19	0	0
Extractives	1.64E-15	1.15E-16	0	0	1.14E-16	0	0
Ethanol	1.863409	0.130438	0.01299	0.01146	0.130438	0.01299	0.01059
H_2O	5011.903	5028.347	5080.69	4990.82	4999.502	5080.70	4963.01
Furfural	4.638444	0.324691	0.03239	0.02958	0.324691	0.03234	0.02729
N_2	0.015566	0.015566	961.778	0.04929	0.015566	961.776	0.04899
CO_2	0	5.811234	2.21972	0.00615	5.42521	2.21973	0.00656
O_2	0.006576	0.006572	222.052	0.02232	0.006572	222.052	0.02218
CH_4	0	17.4337	0.07856	8.75E-6	18.78521	0.07856	6.07E-6
Lactic acid	0.009594	0.000671	6.72E-5	6.64E-5	0.000671	6.72E-5	6.11E-5
Acetic acid	6.67637	0.467345	0.04677	0.04603	0.467346	0.04677	0.04236
Oil	1.81E-13	1.27E-14	0	0	1.27E-14	0	0
CSL	1.67E-17	1.67E-17	0	0	1.65E-17	0	0
WNUTR	0.276192	0.276192	0.27992	0.27661	0.276192	0.27992	0.277
H_2S	0	0.000675	0.00060	0.00011	0.000676	0.00060	0
Biomass	0	1.573	2.41597		1.573	2.41598	

The results which are shown in Table 3.29, are consistent enough. Therefore, the reaction yields and design parameters can be applied for IOBB simulation. However, some unit operation blocks such as sludge dehydration and precipitation are used in simulation software according to calculation results. Thus, dewatering calculations are made by manually and design according to calculation results.

Table 3.30 : Consistency results for wastewater treatment.

Components	Consistency (%)		
	Anaerobic outlet	Aerobic outlet	Water
Glucose	99.22		
Soluble lignin	99.50		
HMF	100.00	100.00	91.89
Arabinose	100.00		
Galactose	99.22		
Mannose	98.55		
G.oligomers	99.88		
Cellobiose	99.69		
X.oligomers	100.00		
Mannoolig.	99.83		
Galactoolig.	99.31		
Araboolig.	100.00		
Xylitol	99.91		
Extractives	99.48		
Ethanol	100.00	100.00	92.41
H_2O	99.43	100.00	99.44
Furfural	100.00	99.84	92.27
N_2	100.00	100.00	99.40
CO_2	93.36	100.00	93.34
O_2	100.00	100.00	99.39
CH_4	92.25	100.00	69.38
Lactic acid	100.00	99.97	91.89
Acetic acid	100.00	100.00	91.91
Oil	100.00		
CSL	98.80		
WNUTR	100.00	100.00	99.93
H_2S	99.82	100.00	0.00
Biomass	100.00	100.00	

3.5.5.8 Cogeneration

The design parameters for the cogeneration process based on the study which is published by Eksi & Karaosmanoglu and NREL report [60, 436]. While the combustion reactions are taken from the NREL report, Rankine cycle parameters are taken from Eksi & Karaosmanoglu (2017). The Rankine cycle parameter results of the study and Aspen Plus simulation software are shown in Table 3.31.

Table 3.31 : Literature data and Aspen Plus simulation software results for Rankine cycle.

Parameters	Literature data	Aspen Plus	Consistency (%)
Stream flow (kg/h)	11464.00	11471.00	99.94
Turbine outlet temperature	107.00	107.30	99.72
Pump work (kW)	14	14.1	99.29
Bioheat production (kW)	6956	6991.7	99.49
Thermal power input (kW)	9936	9988.1429	99.48

Rankine cycle results for literature data and Aspen Plus simulation software are identical, and this design is applicable for IOBB simulation. Table 3.32 presents that the consistency between NREL Report and Aspen Plus simulation software is high enough. Thus, combustion side can be applied for IOBB simulation.

Table 3.32 : Literature data and Aspen Plus simulation software results for combustion.

Components	NREL Report (kg/h)	Aspen Plus (kg/h)	Consistency (%)
Glucose	0.63	0.63	100.00
Xylose	6.99	6.99	100.00
Soluble lignin	7.456	7.441	99.80
HMF	1.122	1.1205	99.87
Arabinose	1.67	1.67	100.00
Galactose	1.085	1.083	99.82
Mannose	0.873	0.873	100.00
Glucooligomer	13.53	13.53	100.00
Celobiose	2.77	2.77	99.96
Xylooligomer	4.37	4.37	100.00
Xylitol	8.267	8.267	100.00
Extractives	38.766	38.7314	99.91
Ethanol	0.019	0.019	100.00
H_2O	65282.729	65245.634	99.94
Furfural	0.094	0.094	100.00
H_2SO_4	1.552	1.552	100.00
N_2	206202.519	206015.678	99.91
CO2	65634.546	65601.466	99.95
O_2	10268.986	10268.986	100.00
CH_4	2.784	2.769	99.46
NO_2	60.873	60.874	100.00
Lactic acid	15.902	15.902	100.00
Acetic acid	21.45	21.45	100.00
Glycerol	1.953	1.953	100.00
Succinic acid	5.547	5.536	99.80
DAP	147.452	147.452	100.00
CSL	1249.038	1241.618	99.41
WNUTR	0.093	0.093	100.00
SO_2	100.371	100.057	99.69
Cellulose	13.579	13.5783	99.99
Xylan	4.371	4.371	100.00
Lignin	141.806	141.647	99.89
Cellulase	5.684	5.684	100.00
Biomass	0.561	0.561	100.00
ZYMO	9.522	9.1822	96.43
Arabinan	0.606	0.606	100.00
Mannan	0.324	0.3186	98.33
Galactan	0.402	0.3986	99.15
Ash	4339.509	4314.823	99.43

4. ASPEN PLUS PROCESS SIMULATION OF INTEGRATED ORGANOSOLV BASED BIOREFINERY RESULTS

This chapter presents the results of the simulation of integrated organosolv based biorefinery (IOBB) in Aspen Plus simulation software and For the simulation part, all information and data which are used in Aspen Plus simulation software are described in Chapter 3 and the Aspen Plus simulation software results are in this section.

The 2 case studies are simulated in Aspen Plus simulation software. According to software, required inputs such as feedstocks, chemicals, air, etc., outputs such as products, stack gas emissions and solid wastes, material and energy balances for each process are described in this section.

For simulating IOBB 179 unit operation blocks, 224 material streams, 93 heat streams, and nine work streams are used in Aspen Plus simulation software for each case. While some streams are defined as described as Chapter 3, some streams are calculated by Aspen Plus simulation software. In this section, calculated stream results are presented.

4.1 Inputs

The term of input defines all materials which are required for IOBB. The feedstock process which is described in Chapter 3. According to Aspen Plus simulation software results, Table 4.1 shows the required inputs which are calculated by Aspen Plus simulation software for IOBB.

4.2 Outputs

The outputs contain the number of final products, stack gas emissions, solid wastes, and wastewater. Bioethanol, organosolv lignin, furfural, acetic acid, bioheat, and biopower are the products of the IOBB. Stack gas emissions contain GHG such as CO_2, CH_4, SO_2, etc. Ash is the solid waste of the IOBB. Wastewater is the process of water after treatment.

Table 4.1 : Calculated inputs by Aspen Plus simulation software.

Inputs	CS-1 (kg/h)	CS-2 (kg/h)
Air	19957	19957
Bark	500	450
Wood	5000	5000
Cellulase	53	39
CNUTR	10	10
CSL	43	42
DAP	1	1
Ethanol	46	45
H_2SO_4	64	63
NH_3	4	4
Oil	12	12
SO_2	4	4
Undecane	0.018	0.015
Water	21400	21545
WNUTR	7	7

4.3 Products and Wastes

The storage unit is designed to collect all products in one place in the simulation. Therefore, this section is the results of the storage unit. The products of IOBB which are calculated by Aspen Plus simulation software are listed in Table 4.2 below.

Table 4.2 : Products of IOBB.

	CS-1	CS-2
Bioethanol (kg/h)	1160	1155
Organosolv lignin (kg/h)	908	894
Furfural (kg/h)	340	358
Acetic acid (kg/h)	122	135
Bioheat (kW)	7495	7223
Biopower (kW)	2139	2064

According to Table 4.2, production quantities in 2 cases have not a significant difference. Bioethanol, organosolv lignin, bioheat and biopower production are higher at Case 1. However, furfural and acetic acid production are higher in Case 2. While, organosolv lignin, furfural, and acetic acid are sent to markets, directly. Ethanol, bioheat, and biopower are used for IOBB requirements, firstly. The requirements of the IOBB are 46.33 kg/h of ethanol, 2826.783 kW bioheat and 993 kW biopower for Case 1 and 45.56 kg/h of ethanol, 2525.051 kW bioheat and 995 kW biopower for Case 2.

4.3.1 Solid wastes

The only solid waste generated by organosolv biorefinery is ash and uncombusted solids from the cogeneration process. The other solids such as tar, bark, wastewater sludge, etc. which are produced in IOBB are combusted in furnaces to obtain biopower and bioheat at cogeneration process. Therefore, the total amount of solid wastes in IOBB is 35.734 kg/h for Case 1 and 47.18 kg/h for Case 2 and obtained these results from material stream 210 (S210) in cogeneration process.

4.3.2 Stack gas emissions

Gasmix unit is designed to collect all stack gases in one place, and it is also called the gas collector. Stack gases are released at 25.6 °C at 1 atm. All stack gases and total stack gas emissions are shown in Table 4.3.

Table 4.3 : Stack gas emissions.

	CS-1 (kg/h)				CS-2 (kg/h)			
	S106	S165	S217	TOTAL	S106	S165	S217	TOTAL
Ethanol	trace	7.35	< 0.001	7.35	trace	7.35	< 0.001	7.35
H_2O	2.05	40.12	5.51	47.67	2.07	40.08	5.37	47.51
Furfural	0.00	< 0.001	< 0.001	0.00	0.00	< 0.001	< 0.001	0.00
H_2SO_4	trace	< 0.001	trace	< 0.001	trace	< 0.001	trace	< 0.001
N_2	86.90	24.42	15956	16067	86.90	24.42	15576	15687
CO_2	12.17	1060	3617	4689	13.74	1058	3466	4538
O_2	14.43	11.73	1871	1898	13.31	11.84	1847	1872
CH_4			0.40	0.40			0.40	0.40
NO			3.93	3.93			3.56	3.56
NO_2			0.12	0.12			0.11	0.11
NH_3	1.44	0.16		1.59	1.40	0.15		1.55
Lactic acid	trace	0.001	0.01	0.01	trace	0.001	0.01	0.01
Acetic acid	0.01	0.01	0.001	0.02	0.01	0.01	0.001	0.02
Glycerol	trace	trace	< 0.001	< 0.001	trace	trace	< 0.001	< 0.001
Succinic acid	trace	trace	< 0.001	< 0.001	trace	trace	< 0.001	< 0.001
SO_2	3.26	0.45	16.47	20.18	3.25	0.45	16.98	20.68
H_2S			0.34	0.34			0.31	0.31
CO			0.003	0.003			0.003	0.003
Levulinic acid	trace	< 0.001	0.003	0.003	trace	< 0.001	0.003	0.003
Formic acid	trace	< 0.001	0.02	0.02	trace	< 0.001	0.02	0.02
Total kg/hr	120.25	1144	21471	22736	120.67	1142	20916	22179

Results in Table 4.3 are given with kg/h unit. However, mg/m^3 is more applicable for air pollution control, and limits are defined as mg/m^3. Therefore, the volumetric flow and density are 5060.498 L/sec and 0.078 L/ft^3, respectively for Case 1 and 4967.652 L/sec and 0.078 L/ft^3, respectively for Case 2. As a result, Table 4.4 gives the total gas emissions with unit mg/m^3.

Table 4.4 : Total gas emissions in mg/m^3 unit.

	CS-1		CS-2	
	kg/h	mg/m^3	kg/h	mg/m^3
Ethanol	7.35	1.11	7.35	0.91
H_2O	47.67	7.21	47.51	5.87
Furfural	0.00	0.00	0.00	0.00
N_2	16067.36	2429.40	15687.15	1937.45
CO_2	4688.98	708.98	4538.11	560.48
O_2	1897.53	286.91	1872.07	231.21
CH_4	0.40	0.06	0.40	0.05
NO	3.93	0.59	3.56	0.44
NO_2	0.12	0.02	0.11	0.01
NH_3	1.59	0.24	1.55	0.19
Lactic acid	0.01	0.00	0.01	0.00
Acetic acid	0.02	0.00	0.02	0.00
SO_2	20.18	3.05	20.68	2.55
H_2S	0.34	0.05	0.31	0.04
CO	0.00	0.00	0.00	0.00
Levulinic acid	0.00	0.00	0.00	0.00
Formic acid	0.02	0.00	0.02	0.00
Total	22735.50	3437.63	22178.85	2739.21

4.3.3 Wastewater

In IOBB simulation, wastewater stream is defined as S202. The temperature of the wastewater stream is 21.1 ^{0}C at 1 atm. The amount and content of the wastewater streams are shown in Table 4.5. These results are obained in Aspen Plus simulation software with the units of kg/h. However, the unit of mg/L is used in wastewater calculations oftenly. Then all results are converted the unit of mg/L and presented.

In addition, COD quantities are important parameter for wastewater treatment process. Therefore, COD quantities are presented in Table 4.6. According to Table 4.6, the contamination of wastewater streams is reduced to regulatory limits which were stated in Chapter 2. This wastewater treatment design is assumed to be efficient and applicable.

4.4 Material Balances

In this section, material balances for each process are shown, individually. Due to having an extended number of unit operation blocks, the material balances are not shown individually for each block. However, individual material streams are presented in Appendix A and B.

Table 4.5 : Wastewater stream contents.

	CS-1		CS-2	
	kg/h	mg/L	kg/h	mg/L
Glucose	0.01	0.34	0.01	0.34
Xylose	0.01	0.40	0.01	0.40
HMF	0.04	2.07	0.03	1.94
Arabinose	0.02	1.09	0.02	1.03
Galactose	0.01	0.34	0.01	0.80
Mannose	0.01	0.52	0.01	0.46
Glucooligomers	0.10	5.75	0.10	5.59
Cellubiose	0.03	1.72	0.03	1.65
Xylitol	0.01	0.40	0.01	0.40
Extractives	0.34	19.26	0.31	17.90
Ethanol	0.01	0.80	0.01	0.80
Water	17299	994474	17448	994619
Furfural	0.01	0.69	0.01	0.74
H_2SO_4	40.49	2327.54	39.28	2238.92
N_2	0.27	15.29	0.27	15.28
CO_2	0.06	3.62	0.06	3.59
O_2	0.14	7.93	0.14	7.92
NO_2	0.28	15.87	0.26	14.76
NH_3	5.45	313.53	5.05	287.70
Lactic acid	0.43	24.89	0.43	24.63
Acetic acid	0.32	18.17	0.33	18.53
Glycerol	0.03	1.90	0.03	1.82
Succinic acid	0.06	3.22	0.06	3.14
DAP	0.65	37.25	0.64	36.48
Oil	0.12	6.73	0.11	6.50
CSL	0.35	20.29	0.35	19.95
Wnutrient	7.54	433.22	7.54	429.58
SO_2	0.26	14.95	0.26	14.88
H_2S	0.01	0.80	0.01	0.68
Levulinic acid	0.03	1.67	0.03	1.54
Formic acid	0.00	0.17	0.00	0.17
Soluble ash	0.02	1.32	0.04	2.00
Total	17356.16	997755.60	17503.84	997778.90

4.4.1 Organosolv pretreatment process

In organosolv pretreatment seven inlet streams and five outlet streams are available. The flow rate of total inlet streams are 49765.45 kg/h, and 49930.01 kg/h, the flow rate of total outlet streams are 49765.45 kg/h and 49930.01 kg/h for CS-1 and CS-2, respectively. As it is seen that, inlet and outlet streams are in balance in organosolv pretreatment. Figure 4.1 presents the material balance of organosolv pretreatment process.

Table 4.6 : COD quantities (mg/L) in wastewater.

	Before Anaerobic Digestion		Before Aerobic Digestion		Process Water	
	CS-1	CS-2	CS-1	CS-2	CS-1	CS-2
Glucose	55.23	53.17	3.91	3.76	0.39	0.38
Xylose	60.37	63.14	4.27	4.47	0.43	0.45
HMF	438.86	418.27	31.06	29.60	3.12	2.98
Arabinose	167.75	151.91	11.87	10.75	1.19	1.08
Galactose	52.18	120.73	3.69	8.54	0.37	0.86
Mannose	77.51	70.21	5.49	4.97	0.55	0.50
Glucooligomers	962.62	926.75	68.13	65.58	6.85	6.60
Cellobiose	275.79	265.51	19.52	18.79	1.96	1.89
Xylitol	62.34	65.24	4.41	4.62	0.44	0.46
Ethanol	274.51	270.07	19.31	18.99	1.73	1.71
Furfural	179.52	190.82	12.65	13.45	1.18	1.25
Lactic acid	3732.42	3693.74	264.17	261.36	26.58	26.29
Acetic acid	2734.68	2790.44	193.51	197.40	19.41	19.80
Glycerol	324.45	310.59	22.96	21.98	2.31	2.21
Succinic acid	427.48	421.21	30.26	29.80	3.04	3.00
Oil	389.42	377.66	27.56	26.72	19.41	18.82
CSL	21.31	20.96	21.55	21.19	21.69	21.32
Levulinic acid	190.90	180.61	13.51	12.78	1.36	1.29
Formic acid	9.90	9.34	0.70	0.66	0.07	0.07
Cellulose	23.44	22.56	1.66	1.60	0.00	0.00
Xylan	38.36	40.14	2.72	2.84	0.00	0.00
Lignin	179.28	175.05	12.69	12.39	0.00	0.00
Cellulase	512.42	380.97	36.27	26.96	0.00	0.00
Biomass	14.38	15.79	591.77	579.61	0.00	0.00
Zymo	359.01	355.96	25.41	25.19	0.00	0.00
Acetate	6.51	7.26	0.46	0.51	0.00	0.00
Arabinan	16.16	14.64	1.14	1.04	0.00	0.00
Mannan	34.72	31.46	2.46	2.23	0.00	0.00
Galactan	0.09	0.22	0.01	0.02	0.00	0.00
COD	11621.61	11444.40	1433.11	1407.77	112.11	95.75

At organosolv pretreatment, inlet streams are S1 (make-up solvent), S2 (woody biomass), S3 (catalyst), S19 (washing water), S23 (water for precipitation oforganosolv lignin), S28 (washing water) and S44 (recycling streams of solvent and water from solvent recovery). The outlet streams of organosolv pretreatment are S12, S16, S21, S33, and S35. S12 is solid rejects which sent to cogeneration part for combustion. S16 and S35 are solvent rich streams and sent to the furfural production process for solvent recovery. S21 is sugar rich solution and sent to saccharification and fermentation process for sugar to ethanol conversion, and lastly, S33 is produced organosolv lignin stream which contains 99.95% of organosolv lignin and 0.05% of monomeric sugars.

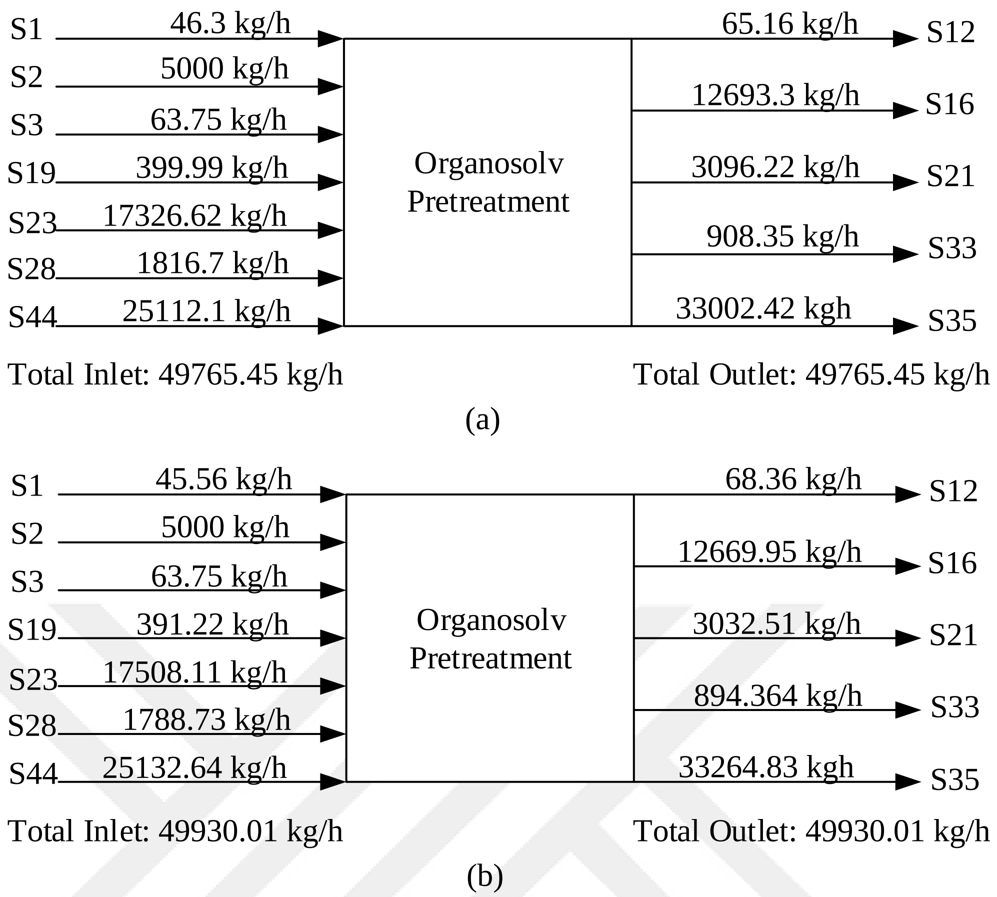
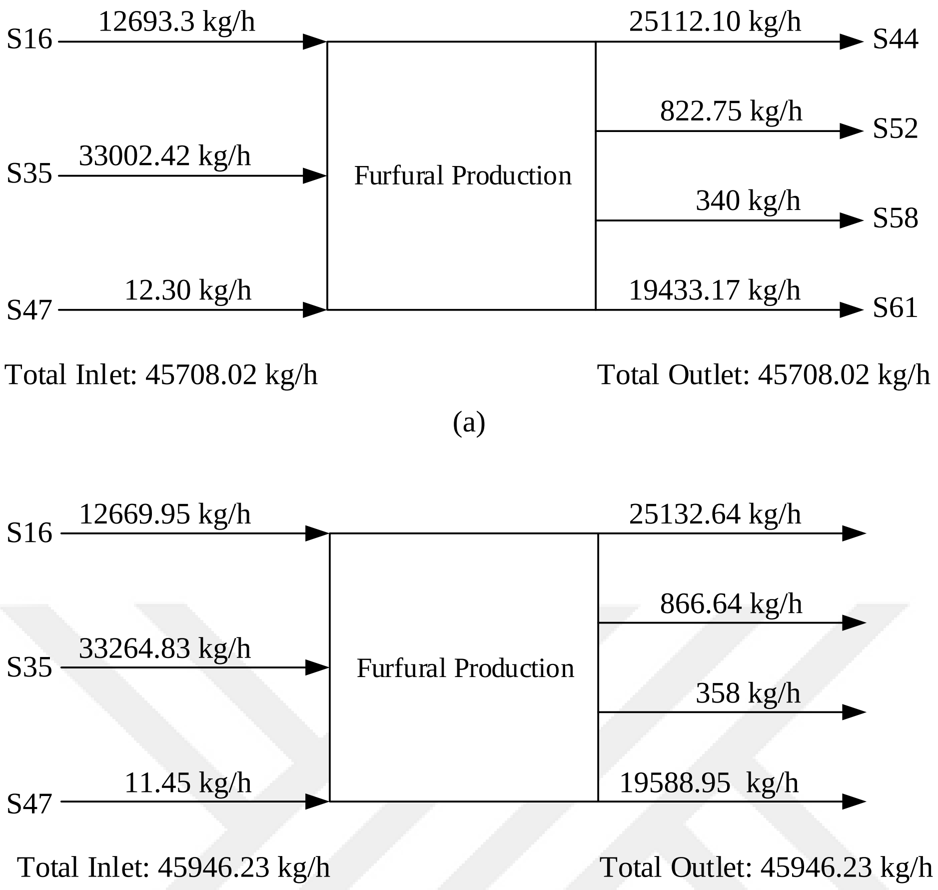


Figure 4.1 : Material balance of organosolv pretreatment process for (a) CS-1 and (b) CS-2.

4.4.2 Furfural production process

Furfural production process contains solvent recovery and furfural production from xylose. There are three inlet streams, and four outlet streams are found in the furfural production process. The furfural production material flows are in balance and inlet and outlet streams for CS-1 and CS-2 are calculated as 45708.02 kg/h and 45946.23 kg/h, respectively. Figure 4.2 shows the material balance of furfural production process.

The inlet streams S16 and S35 are obtained from organosolv pretreatment. S47 is H2SO4 catalyst which is used for xylose to furfural conversion. The outlet stream S44 is solvent recovery stream and contains ethanol and water. It is sent to organosolv pretreatment process for reducing solvent cost. S52 is sugar rich solution, and it is sent to the enzyme production process. S58 has produced furfural streams and sent to storage process for selling. Finally, S61 is an acetic acid rich solution that also contains other inorganic acids sent to the acetic acid recovery process.



(a)

(b)

Figure 4.2 : Material balance of furfural production process for (a) CS-1 and (b) CS-2.

4.4.3 Acetic acid recovery process

The acetic acid process contains two inlet streams and three outlet streams. The material balance is provided in CS-1 and CS-2. For CS-1, the total input and output stream is 19462.275 kg/h, while for CS-2, it is 19621.692 kg/h. Figure 4.3 indicates the material balances of the acetic acid recovery process.

As it is seen in Figure 4.3, inlet streams of acetic acid production are S61 and S62. S61 is inorganic acid solutions which contain mostly acetic acid and in small quantities of formic acid, levulinic acid, lactic acid, and succinic acid. S62 is make-up TOPO and undecane solution which required for extraction. The outlet streams S69 is raffinate phase of acetic acid extraction and includes mostly water. It is sent to the wastewater treatment process for water recovering. S77 is distillate phase of acetic acid extraction. S77 is used for cogeneration process for combustion. In the end, S79 is a product stream which contains acetic acid.

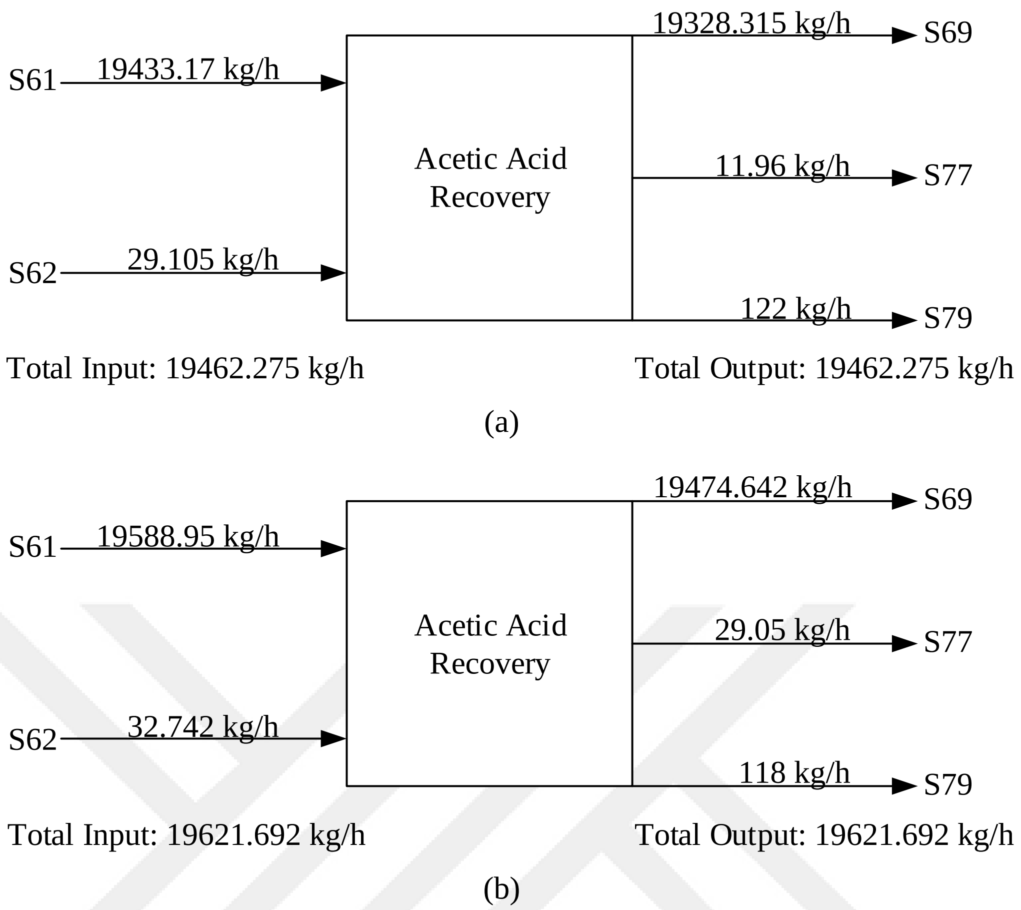


Figure 4.3 : Material balance of acetic acid recovery process for (a) CS-1 and (b) CS-2.

4.4.4 Enzyme production process

The enzyme production process has ten inlet streams and four outlet streams. The material balance is provided for CS-1 and CS-2. The inlet and outlet stream is found as 1120.47 kg/h for CS-1 and 1162.78 kg/h for CS-2, respectively. Figure 4.4 presents the material balances of the enzyme production process.

The inlet streams of enzyme production process are S52 (sugar-rich solution from furfural production), S84 (sugar-rich solution from distillation process), S86 (ammonia stream for seed fermentation), S87 (CSL stream for seed fermentation), S88 (air stream), S96 (ammonia stream for seed fermentation), S97 (nutrient for fermentation), S98 (CSL stream for seed fermentation), S100 (oil for preventing foaming) and S101 (sugar-rich solution from distillation process). The outlet streams of enzyme production are S80 (sugar solution for distillation process), S106 (exhaust gases), S108 (excess inoculum) and S109 (produced enzyme for saccharification and fermentation).

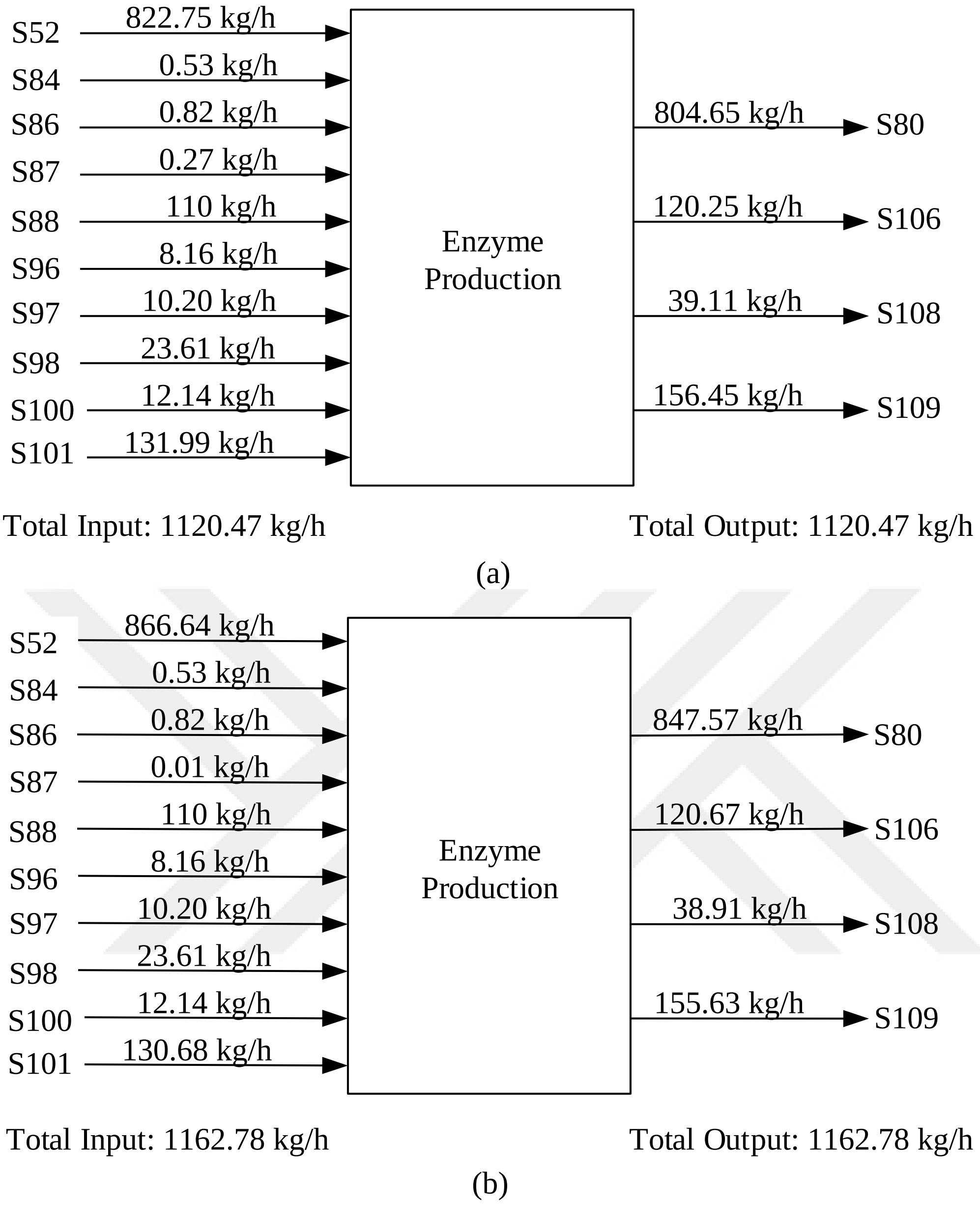


Figure 4.4 : Material balance of enzyme production process for (a) CS-1 and (b) CS-2.

4.4.5 Saccharification and fermentation process

Saccharification and fermentation process includes nine inlet streams from organosolv reaction process, enzyme production process and distillation process. Total inlet and outlet streams are 5950.31 kg/h and 5915.10 kg/h for CS-1 and CS-2, respectively. Figure 4.5 presents the material balances of saccharification and fermentation process.

S21 is sugar rich solution from organosolv pretreatment. S80 is also a sugar-rich solution which is prıduced from enzyme production. S109 is fermented seed streams from the enzyme production process. S112 is enzyme stream for fermentation. S115

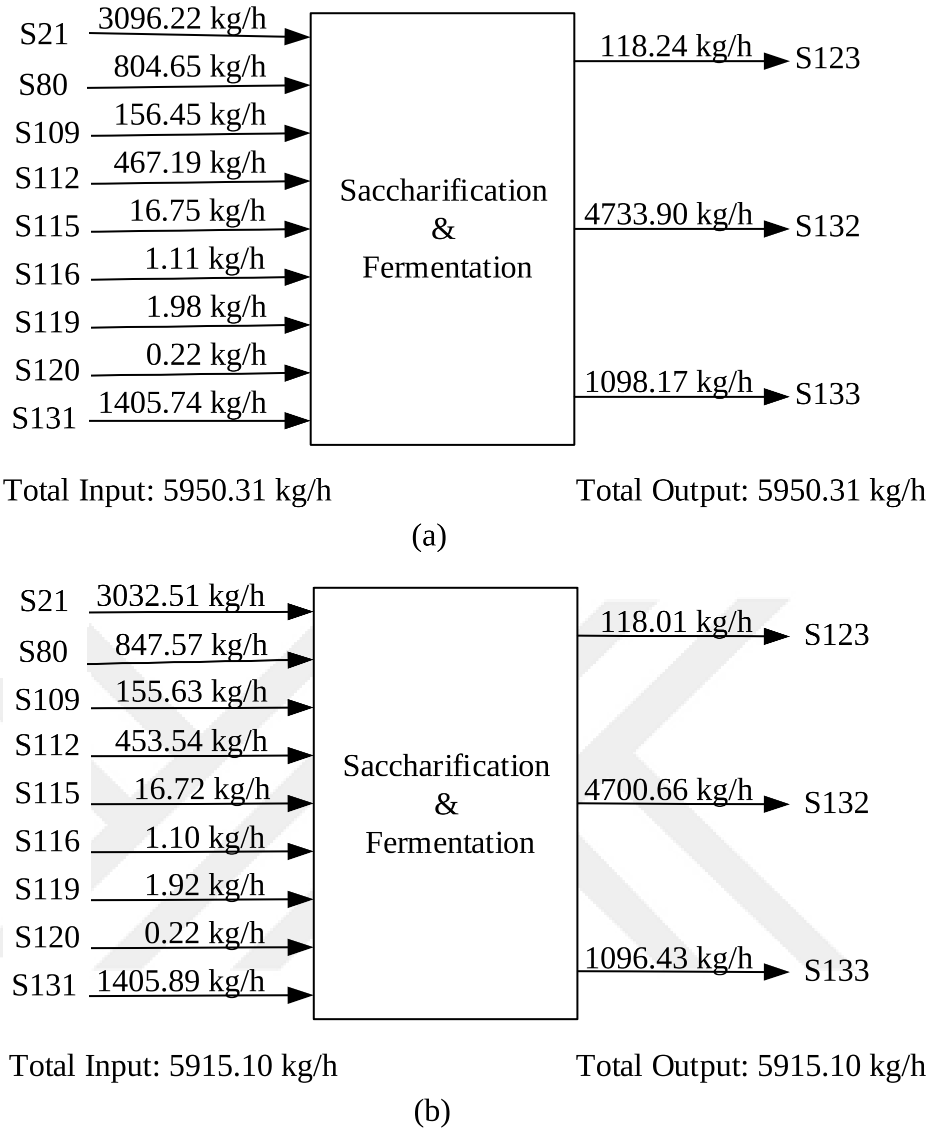
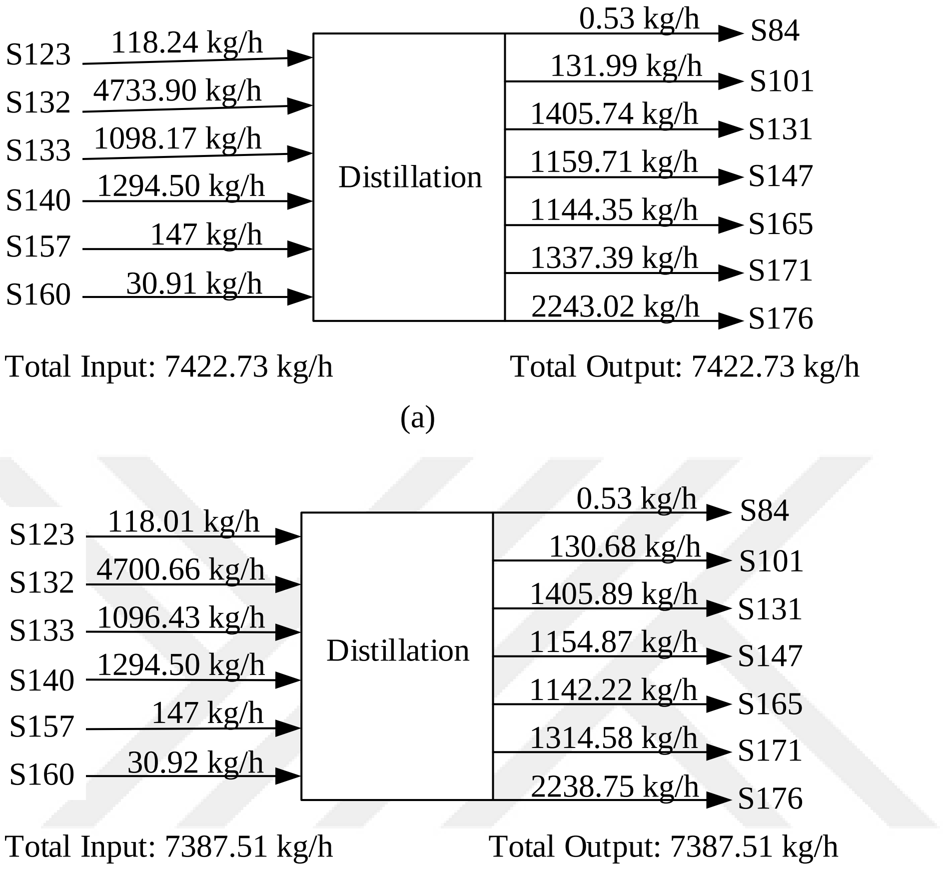


Figure 4.5 : Material balance of saccharification and fermentation process for (a) CS-1 and (b) CS-2.

and S119 are CSL streams, and S116 and S120 are DAP streams. S131 is sugar rich streams produced by the distillation process. Outlet streams S123 and S133 are exhausted gas streams and sent to a distillation process for gas washing before releasing the air. S132 is bioethanol rich stream and sent to a distillation process for purification.

4.4.6 Distillation process

In the distillation process, six inlet streams and seven outlet streams are available. The material balances are provided in the distillation process, and inlet and outlet streams are 7422.73 kg/h for CS-1 and 7387.51 kg/h for CS-2, respectively. The material balances of the distillation process are shown in Figure 4.6.



(a)

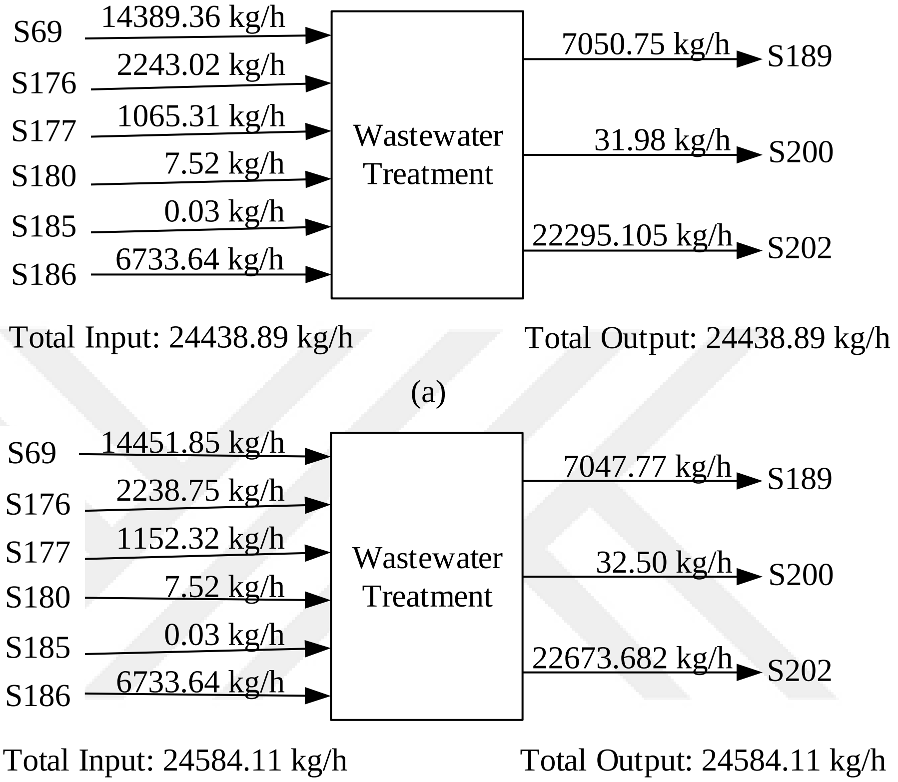
(b)

Figure 4.6 : Material balance of distillation process for (a) CS-1 and (b) CS-2.

The inlet streams S123 and S133 obtained from saccharification and fermentation process. They contained exhaust gases and washed with water and release to the air. S132, water, and bioethanol mixture stream are produced by saccharification and fermentation process and dehydrated to produce pure bioethanol. S157 is a water stream, and S160 is air stream. Outlet streams S84 and S101 are sugar-rich streams which are not converted to bioethanol and send back to enzyme production. S131 is also a sugar-rich solution and send to saccharification and fermentation process for reproducing bioethanol. S147 is dehydrated bioethanol and send to storage for selling to the market. S165 contains exhaust gas emissions and releases to air. S171 is unconverted sugars and send to cogeneration process for combustion. S176 is water-rich stream and send to wastewater treatment.

4.4.7 Wastewater treatment process

There are six input streams and three streams in wastewater treatment. Total input and output streams of wastewater treatment for CS-1 are 24438.89 kg/h and 24584.11 kg/h for CS-2. Figure 4.7 shows the material balances of wastewater treatment.



(a)

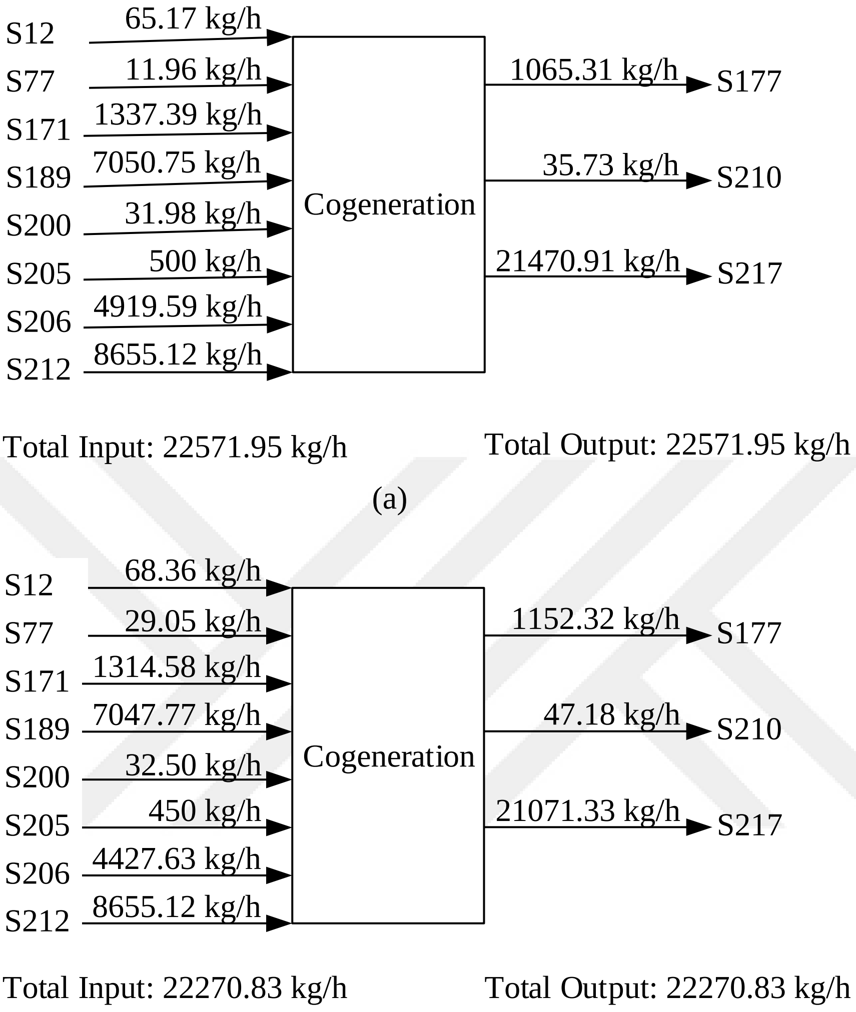
(b)

Figure 4.7 : Material balance of wastewater treatment process for (a) CS-1 and (b) CS-2.

In the wastewater treatment process, inlet streams are S69, S176, S177, S180, S185, and S186. S69 is the raffinate phase obtained from the acetic acid recovery process. S176 and S177 are wastewater stream from distillation and cogeneration. S180 and S185 are nutrient streams that are requiring for anaerobic and aerobic digestion. S186 is air stream for aerobic digestion. Outlet streams are S189, S200 and S202. S189 is the exhaust gases which releases to air. S200 is sludge and send to cogeneration for combustion. At last, S202 is the final wastewater stream.

4.4.8 Cogeneration process

The inlet streams of the cogeneration process consist of 8 streams and outlet streams consist of 3 streams. The total input and output streams of the cogeneration process are 22571.95 kg/h for CS-1, and 22270.83 kg/h for CS-2, respectively. The material balances of the cogeneration process are presented in Figure 4.8.



(a)

(b)

Figure 4.8 : Material balance of cogeneration process for (a) CS-1 and (b) CS-2.

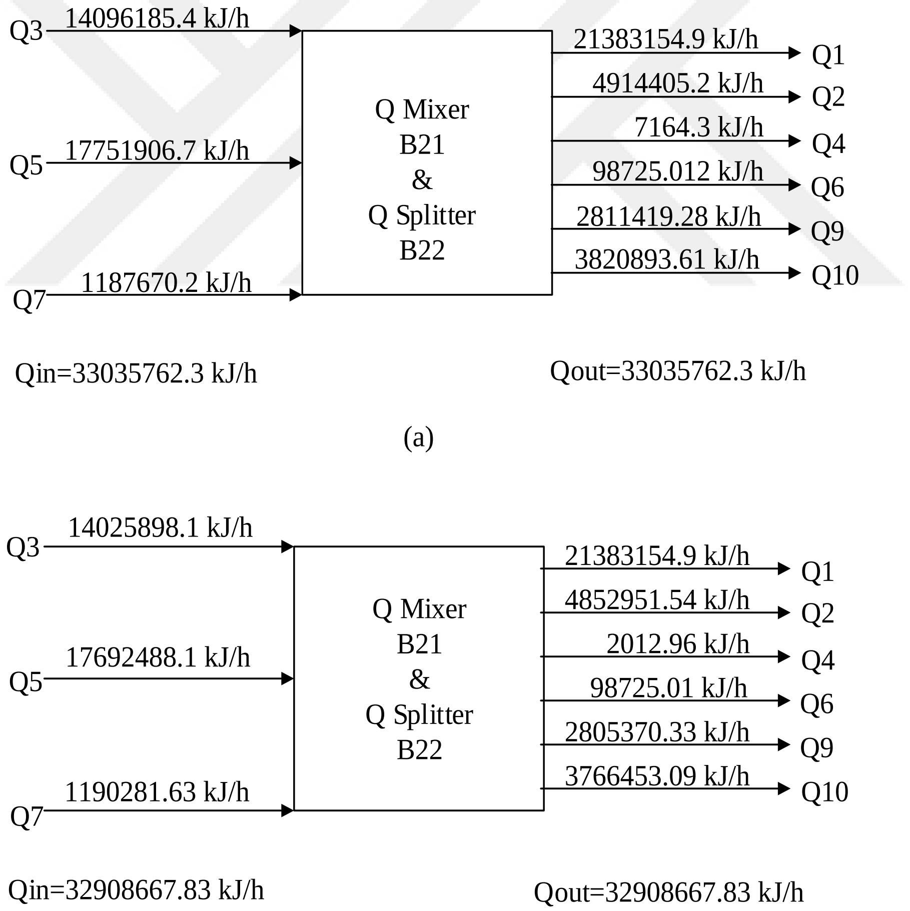
Input streams S12, S77, S171, and S189, are produced by organosolv pretreatment, acetic acid, distillation, and wastewater treatment. S200 is sludge that produced from wastewater treatment. S205 is the bark of SOC, S206, and S212 are air stream which required for combustion. Output streams S177 is wastewater of the cogeneration process and send to wastewater treatment. S210 is ash and other uncombusted solids, and it is the total solid waste of IOBB. S217 is the exhaust gases which occurs from combustion.

4.5 Energy Balances

Energy balances present the heat and work balances between and in the processes. Heat balances are shown as the required and produced heat in the process, and excess heat is sent to the utilities unit for using other processes which have heat requirements. Each process has its heat balances. On the other hand, work streams are directly sent to the utilities unit, and the work requirement is provided by biopower which is produced in the cogeneration process.

4.5.1 Organosolv pretreatment process

The produced heat in the organosolv pretreatment process is a self-sufficient process. Therefore, the difference between produced and consumed heat is sent to the utilities unit. The heat flows for organosolv pretreatment process is shown in Figure 4.9.



(a)

(b)

Figure 4.9 : Heat balances of organosolv pretreatment process for (a) CS-1 and (b) CS-2.

The produced heat streams (Q3, Q5, and Q7) are collected in a heat mixer. Generally, heat is produced for the cooling process and produced heat is used in the heating process. Then splitted for the requirements. Each process assumed to be losing 10% of heat during the process (Q9). The excess heat (Q10) is sent to the utilities unit.

4.5.2 Furfural production process

Furfural production process is heat required process. Figure 4.10, shows all inlet and outlet heat streams in the furfural production process.

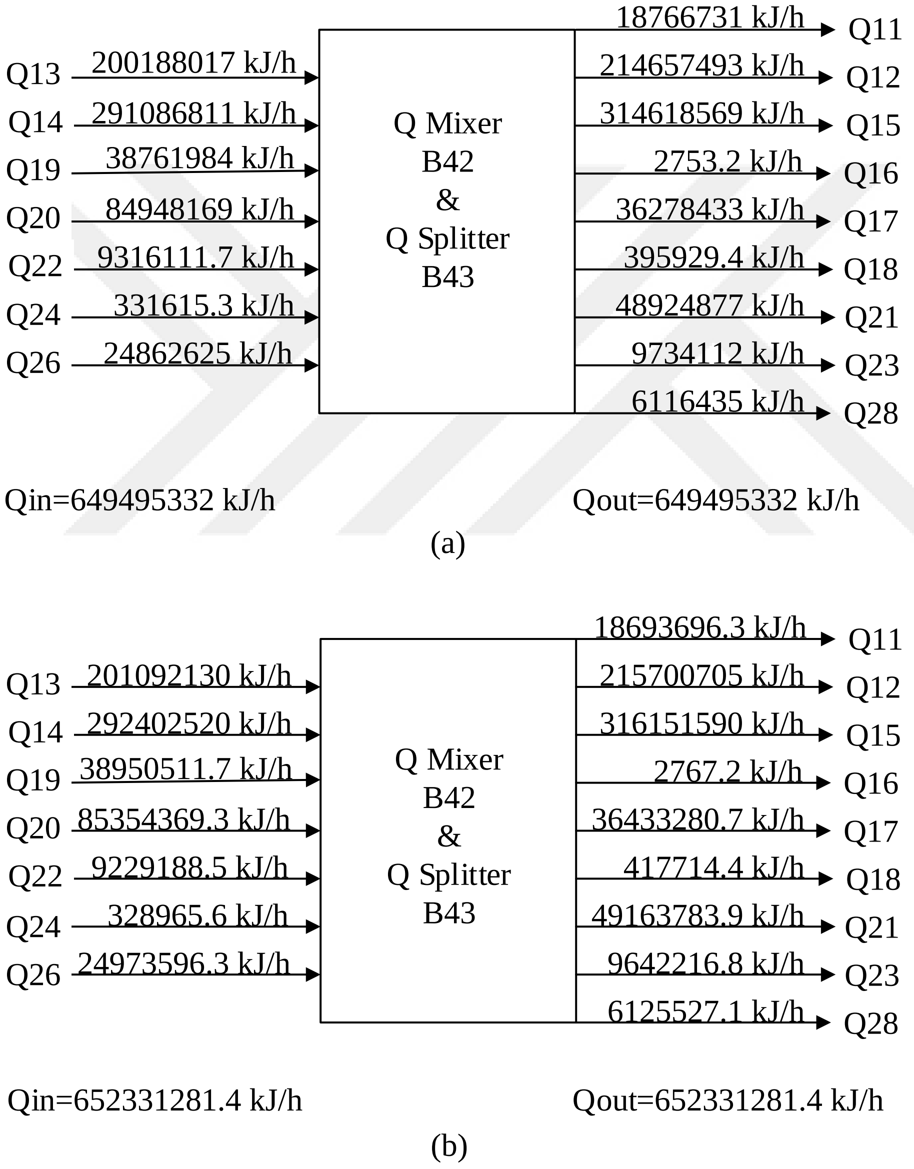


Figure 4.10 : Heat balances of the furfural production process for (a) CS-1 and (b) CS-2.

The heat streams from heat exchangers and distillation columns are mixed in a heat mixer (B42). Additionally, a heat stream (Q26) from utilities unit is added to heat mixer to provide the necessary heat for all unit operation blocks. Next, the outlet heat stream of heat mixer is fed into a heat splitter and total heat is divided by unit operation block’s heat requirements. 10% of heat (Q28) is assumed to be lost in the process. In conclusion, the total input and output heat streams are in balance.

4.5.3 Acetic acid recovery process

The acetic acid recovery process is not a self-sufficient process. Therefore, additional heat stream is required for providing energy balance. Figure 4.11, presents the heat streams and energy balance of acetic acid recovery process.

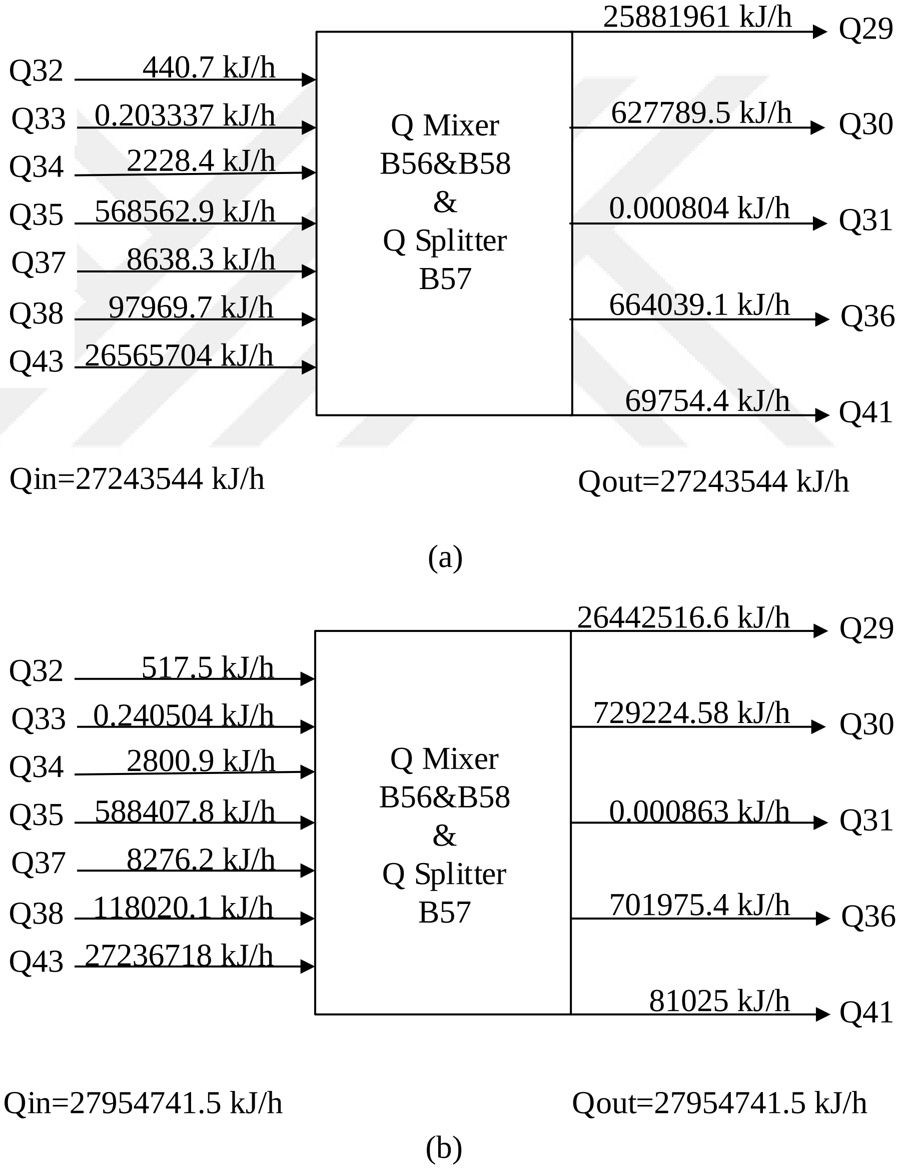


Figure 4.11 : Heat balances of the acetic acid recovery process for (a) CS-1 and (b) CS-2.

Produced heat streams (Q32 to Q38) are obtained from the heat exchanger and distillation blocks (B47, B49, B51, B52, B55, B53). These heat streams and additional heat stream (Q43) from utilities unit are fed into heat mixers (B56 and B58). Total produced heat is 27243544 kJ/h and 27954741.5 kJ/h for CS-1 and CS-2, respectively. The total heat is splitted by a heat splitter (B57) for providing heat requirements of unit operation blocks. 10% of total heat (Q41) is assumed to be lost in the acetic acid recovery process.

4.5.4 Enzyme production process

During enzyme production, heat is produced, and excess heat is sent to the utilities unit for using other processes. Energy balances in the enzyme production process are shown in Figure 4.12.

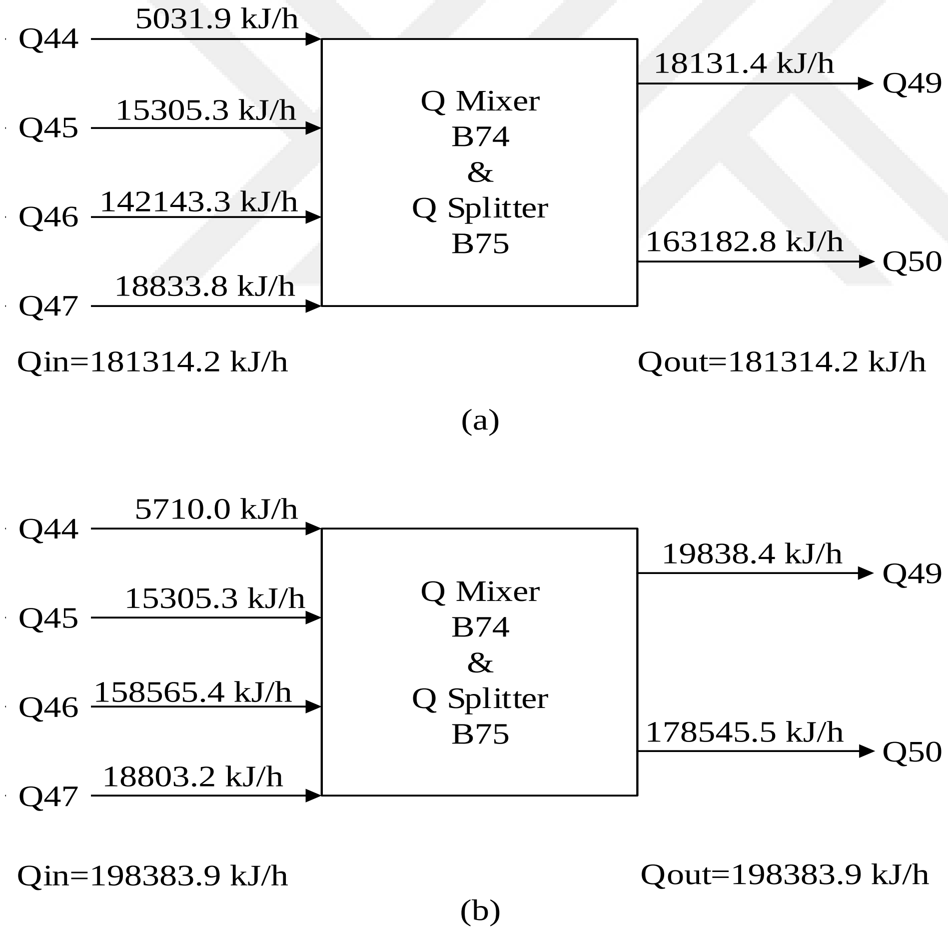
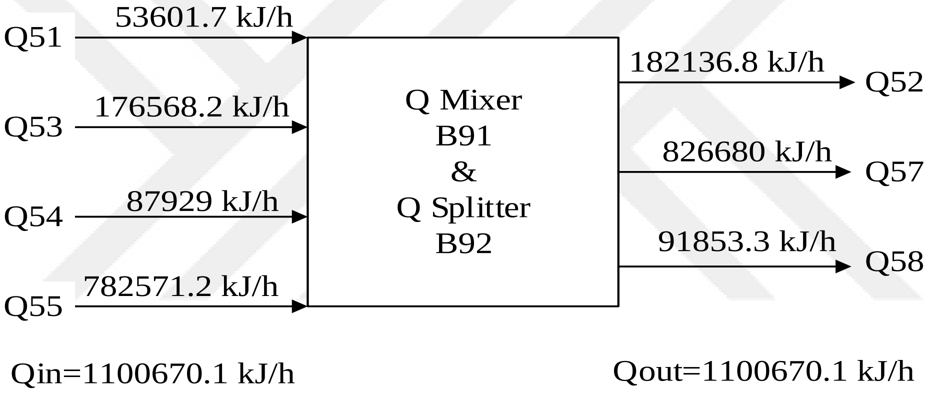


Figure 4.12 : Heat balances of the enzyme production process for (a) CS-1 and (b) CS-2.

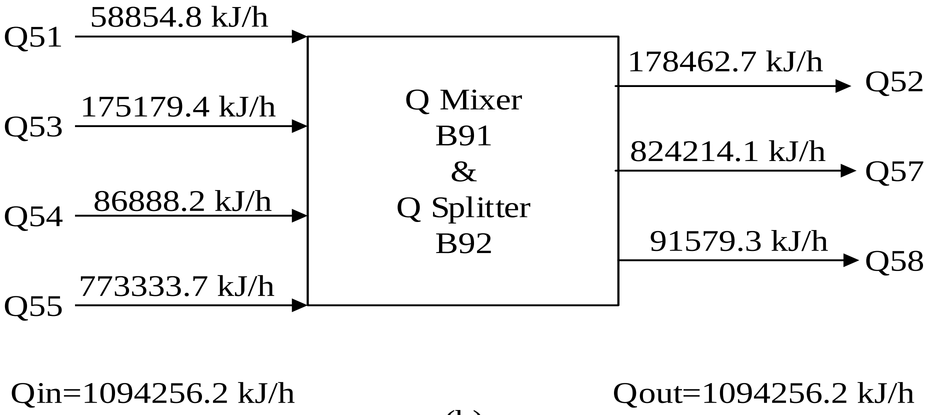
As seen in Figure 4.12, heat is produced by block 60, 64, 66 and 68 (Q44, Q45, Q46, and Q47). While B60 and B66 are reactors, B64 and B68 are heat exchangers. Total produced heat is sent to a heat mixer (B74) and then, fed into a heat splitter (B75) for another heat requirements.10% of total heat (Q49) is assumed to be lost during the enzyme production process, and rest of heat (90%) (Q50) is sent to utilities unit.

4.5.5 Saccharification and fermentation process

Heat is produced during saccharification and fermentation process. Figure 4.13 presents the energy balances of the saccharification and fermentation process. Heat streams (Q51, Q53, Q54, and Q55) are produced by unit operation blocks (B77, B79, B82, and B87). These streams are fed into a heat mixer (B91) and then, total heat is sent to heat splitter (B92). Q57 is sent to B78 reactor to provide heat requirements. Q58 is loss heat and calculated as 10% of total heat. Q57 is excess heat and sent to utilities unit for using other equipment which has heat requirement.



(a)



(b)

Figure 4.13 : Heat balances of saccharification and fermentation process for (a) CS-1 and (b) CS-2.

4.5.6 Distillation process

The distillation process is one of the high heat consumption processes in IOBB. Lots of heat stream is produced and consumed in the distillation process.

Figure 4.14 presents heat balances through the distillation process. As it is seen in Figure 4.14, several heat streams are produced by heat exchangers and distillation columns such as Q60, Q62, Q63, Q66, Q67, Q68, Q69, Q70, Q71 and Q72. These streams are mixed in heat mixers. Total heat production is 6765879.9 kJ/h for CS-1 and 6765804.1 kJ/h for CS-2. This produced heat is sent to heat splitters, and heat is divided into several streams for heat requirements of unit operation block. 10% of heat is assumed to be lost during distillation process in splitter. Q74 and Q77 are defined as lost heat streams.

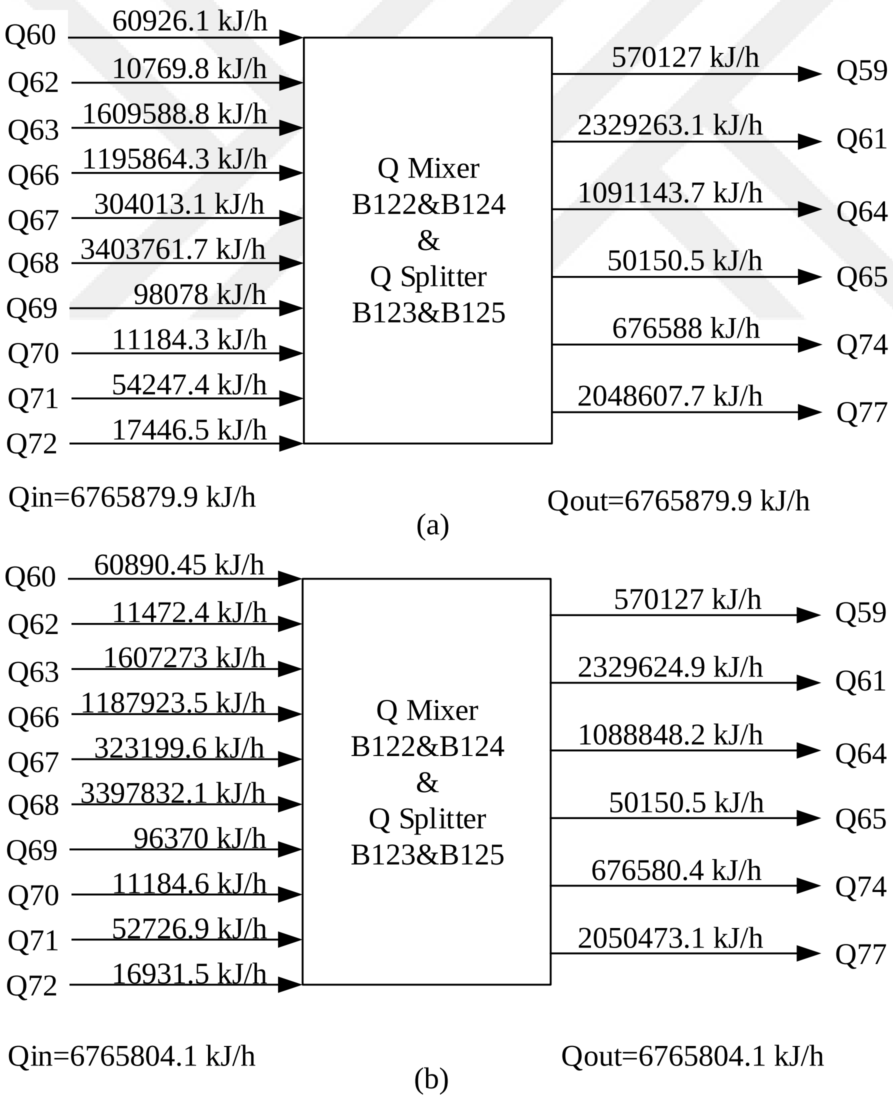
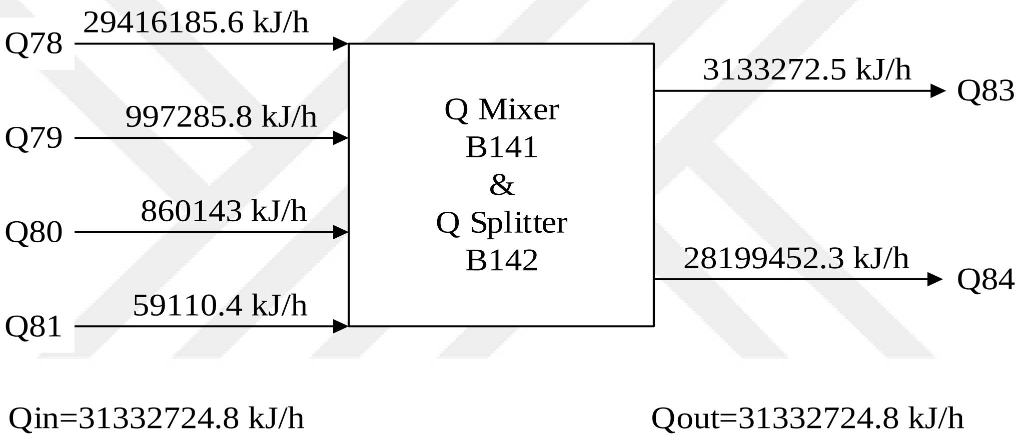


Figure 4.14 : Heat balances of distillation process for (a) CS-1 and (b) CS-2.

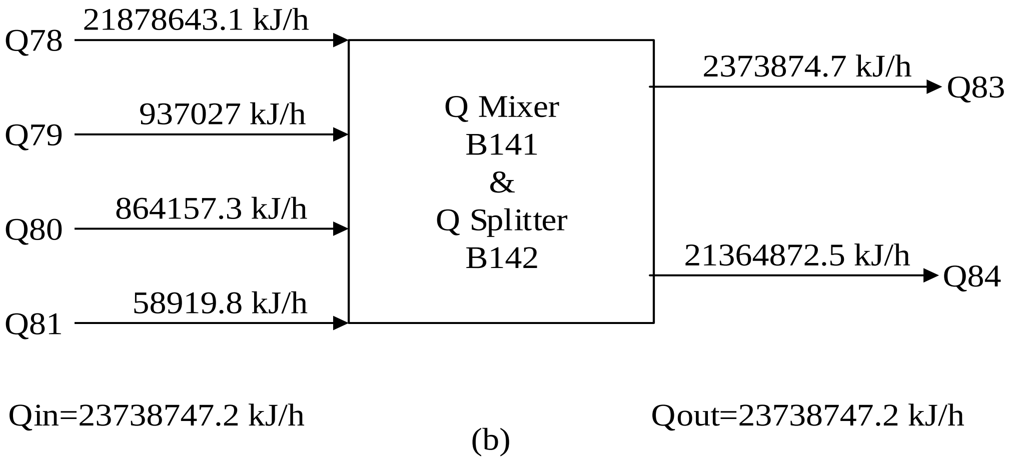
4.5.7 Wastewater treatment process

During wastewater treatment process, several heat streams are produced. Figure 4.15 shows the heat balances in the wastewater treatment process.

In the wastewater treatment process, four heat streams are produced. Q78 heat stream is produced by a heat exchanger (B127), Q79 is produced by anaerobic digestor (B129), Q80 is produced by aerobic digestor (B132) and at last Q81 is produced by a heat exchanger (B139). All produced heat streams are added in a heat mixer (B141), then, fed into a heat splitter (B142). 10% of heat is assumed to be lost in the wastewater treatment process (Q83), and rest of heat (90% of total heat) is defined as Q84 and sent to utilities unit for using another heat required unit operations.



(a)



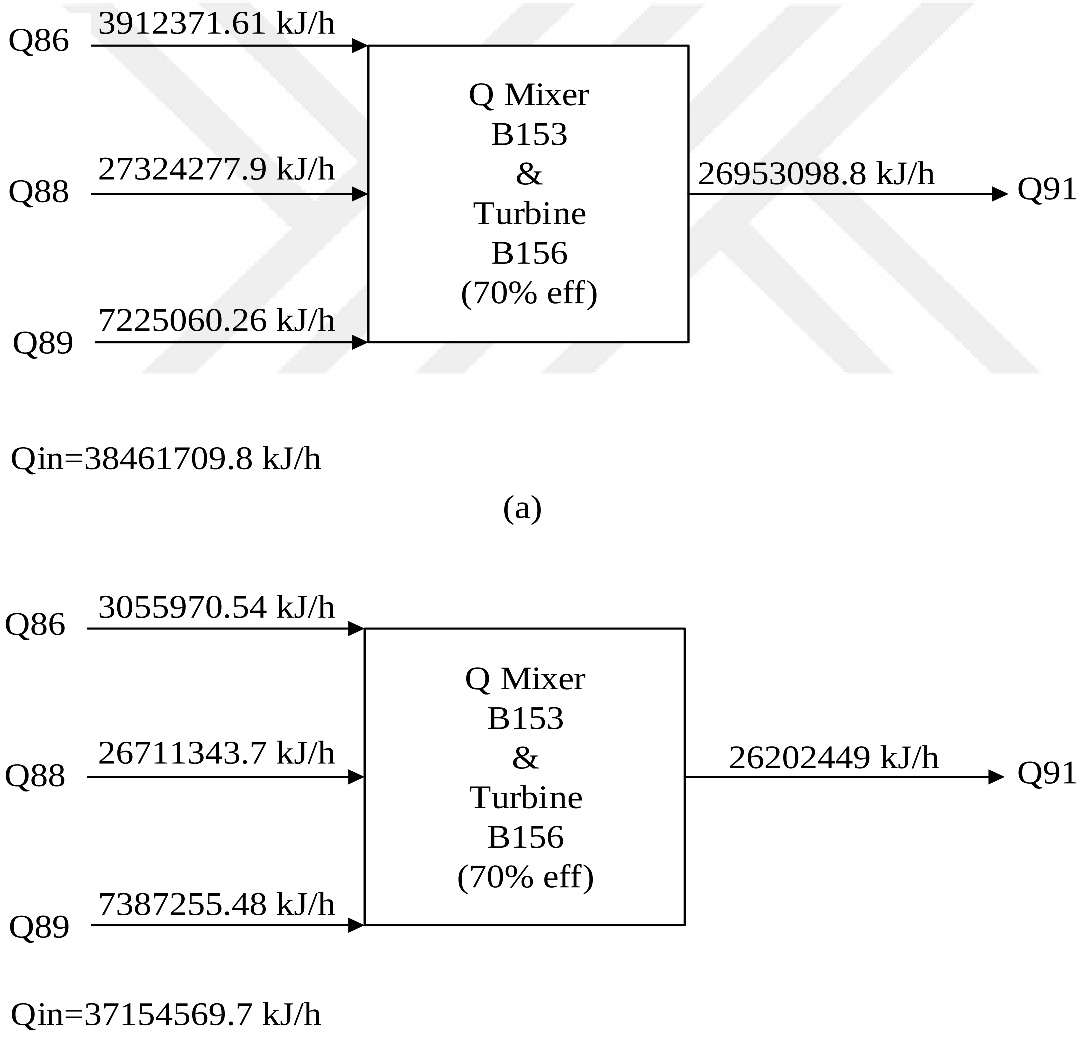
(b)

Figure 4.15 : Heat balances of the wastewater treatment process for CS-1 (a) and CS-2 (b).

4.5.8 Cogeneration process

All processes described above is based on heat generation or consumption. Unlikely other processes, in the cogeneration process, heat is converted to biopower and bioheat by Rankine cycle. The heat balances of the cogeneration process are shown in Figure 4.16.

In the cogeneration process, heat is produced by heat exchangers and Q86, Q88 and Q89 streams are obtained. Then, these streams are fed in a heat mixer. The total heats which are 38461709.8 kJ/h for CS-1 and 37154569.7 kJ/h for CS-2 are sent to the turbine to produce bioheat. Turbine thermal efficiency is set 70%, and bioheat stream are produced as 26953098.8 kJ/h for CS-1 and 26202449 kJ/h for CS-2.



(a)

(b)

Figure 4.16 : Heat balances of the cogeneration process for (a) CS-1 and (b) CS-2.

4.5.9 Utilities unit

In the utilities unit, all excess heat and power streams are mixed and sent to other heat or work required processes. Heat and work energy balances of the utilities unit are shown in Figure 4.17 and Figure 4.18**.**

All consumed work which has positive value and biopower which has negative value are mixed in a work mixer (B162). Then, total work is fed into work splitter (B163) and divide the stream as the IOBB requirements. W8 is the IOBB work requirement and fed back to the biorefinery. The rest of the work (W9) is the excess work s defined as product and sent to grid.

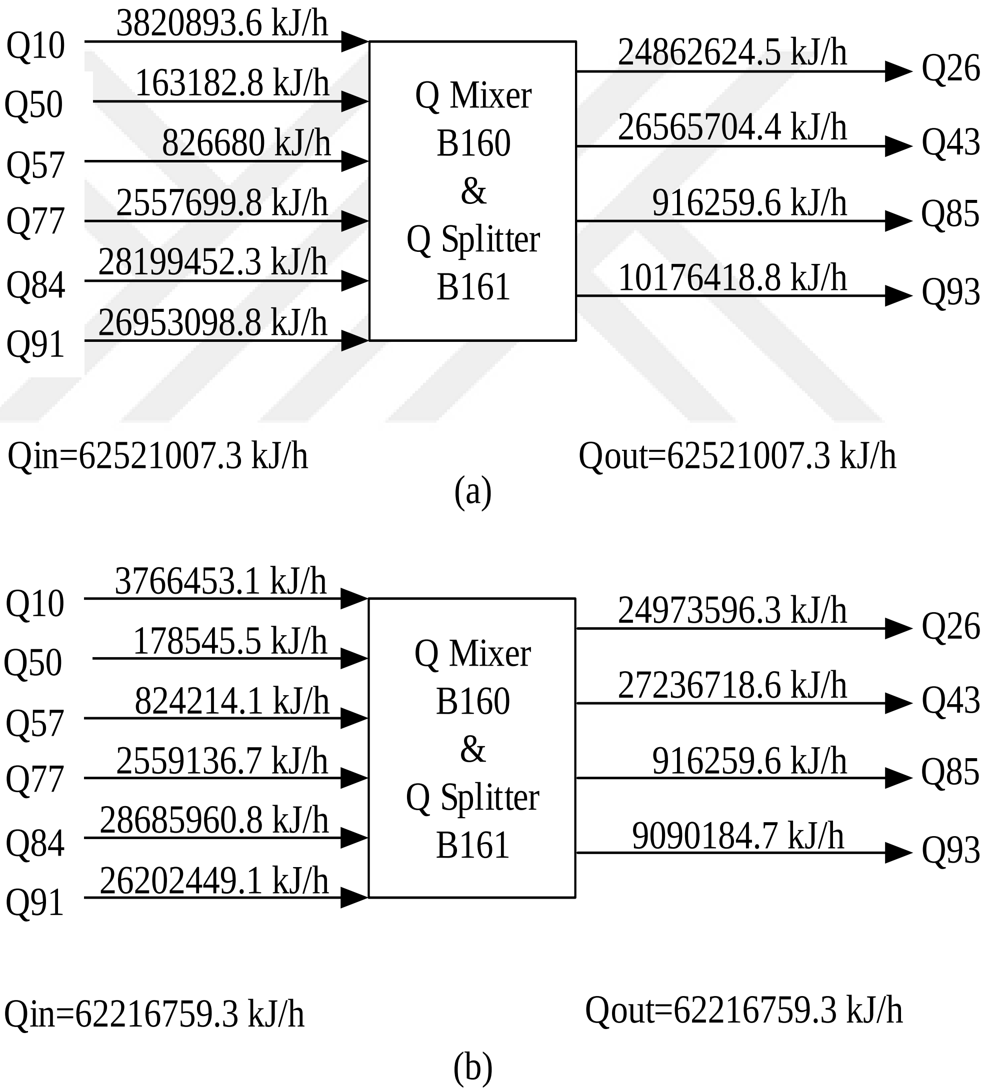
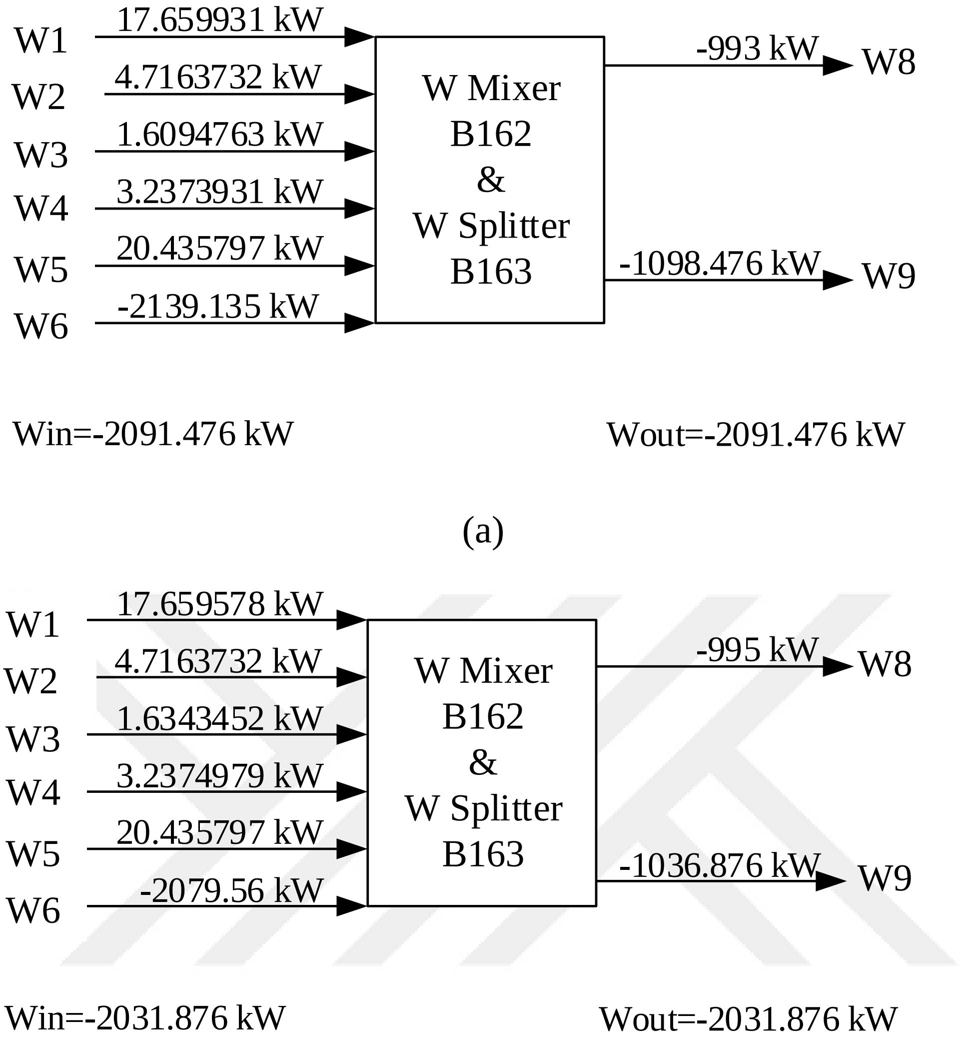


Figure 4.17 : Heat balances of utilities unit for (a) CS-1 and (b) CS-2.



(a)

(b)

Figure 4.18 : Work balances of utilities unit for (a) CS-1 and (b) CS-2.

5. LIFE CYCLE ASSESSMENT OF INTEGRATED ORGANOSOLV BASED BIOREFINERY UTILIZING SESSILE OAK (*Quercus petraea*) COPPICES AND INDUSTRIAL WOOD SAWDUST

This chapter involves the goal and scope definition, inventory analysis section for LCA study of integrated organosolv based biorefinery (IOBB) utilizing sessile oak (*Quercus petraea*) coppices and industrial wood sawdust. Case studies are explained and simulated in Chapter 3, and the results were given in Chapter 4.

The aim of this chapter is present to selections of methodology and preparation of detailed inventory data for the LCA of IOBB with the subtitles of goal and scope definition of LCA study and inventory analysis of LCA study. All selections, data, and assumptions are presented as clearly as possible.

5.1 Goal and Scope Definition of the LCA Study

The first step of the LCA study is determined the methodological choices according to LCA standards [55, 56], SimaPro software tutorials and manuals and other studies that found in the literature. These selections and assumptions are presented in this section.

5.1.1 Goal

The goals of the LCA study of IOBB are;

- To develop an IOBB in term of environmental aspects. Resource requirements, energy requirements and environmental loadings are analyzed and compared with literature resources.
- To analyze the subsystems in the system boundary according to energy requirements, resource requirements or generation of pollutants and identify the environmental burdens for each subsystem.
- To contribute to the literature and provide information and directions to decision-makers, investors, academics and policymakers.
- To define the most environmental system in researched systems.

5.1.2 Scope

Scope definition includes the system boundary, functional unit, modeling approach, allocation selection, impact assessment methods, impact categories, and required specificity and all selections are determined in the subtitles.

5.1.2.1 System boundary

System boundary started with the transportation of feedstock from the forest for SOC and timber manufacturer for IWS and finished with the production of biorefinery products. System boundary selection is presented in Figure 5.1. Cradle to gate approach is not selected for IOBB because of being a wide variety of IWS. IWS is collected from different countries, occurred from different species and produced from different processes. Thus, forest activities and manufacturing of IWS are not comparable with other studies. Therefore, forest activities are not included in LCA studies.

System boundary includes:

- Transportation of feedstocks from forest or manufacturer to IOBB
- Transportation of chemical from seller to IOBB
- IOBB
    - Organosolv pretreatment
    - Furfural production
    - Acetic acid recovery
    - Enzyme production
    - Saccharification and fermentation
    - Distillation
    - Wastewater treatment
    - Cogeneration

System boundary begins with transportation of feedstocks such as chemicals, oak coppices, and industrial wood sawdust. Chemicals are bought from a nearest chemical distributor company in Bursa, and located 44 km away from the designated biorefinery location. Oak coppices are assumed to be 50 km away from the biorefinery. Industrial wood sawdust is produced in Inegol/Bursa, and the location of manufacturers is 15 km away from the biorefinery. After the transportation of feedstocks, biorefinery plant is sttarted and includes organosolv pretreatment process, furfural production, acetic acid

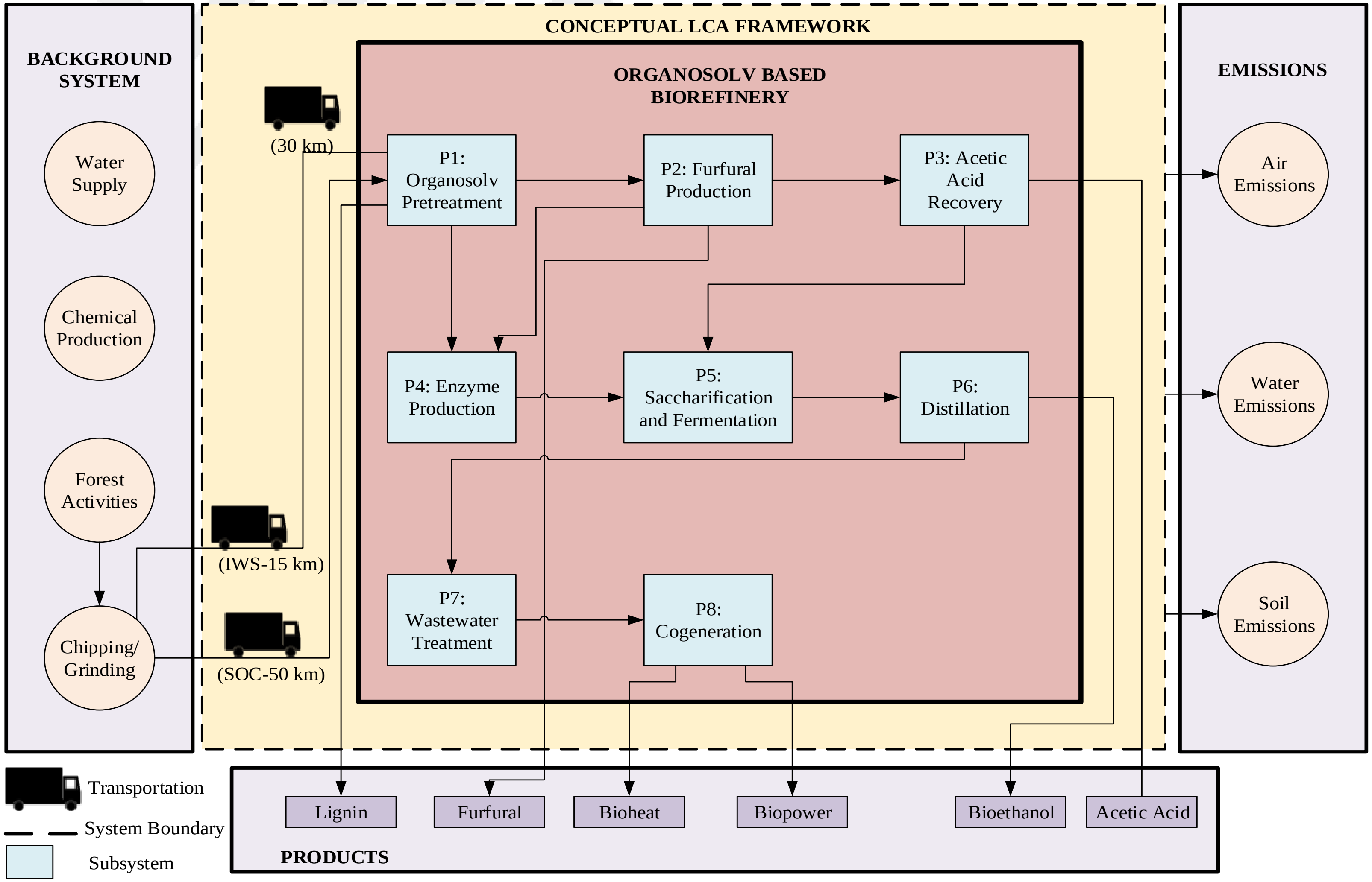


Figure 5.1 : System boundary of the LCA study of IOBB.

recovery, enzyme production, saccharification and fermentation, distillation, wastewater, and cogeneration process. Then, product and ash storage is included in the system boundary. Ash transport from biorefinery to the forest is assumed 50 km. At last, ash spreading is the last point in system boundary. Product transportation and usage are not included in the system boundary.

CS-1 and CS-2 are defined in the previous section. CS-3 is a literature study which was published by Kautto et al. (2013) [285]. At their study, organosolv based biorefinery (not integrated) was investigated. The products are bioethanol, organosolv lignin, acetic acid, furfural, and biopower. The main parameters of selection of this literature study, all material balances are available on SpringerLink, and same products are produced. Although process differences exist, it is available for LCA comparison. At this study, the feedstock of organosolv pretreatment is 83.33 MT/h; furfural recovery was selected instead of furfural production, enzyme production and wastewater treatment were not modeled, cogeneration exhaust gases were not determined. Bioheat is not self-sufficient at their simulation. Therefore, bioheat was not produced as a product. Table 5.1 gives general information about CS-3.

Table 5.1 : General input and output streams of CS-3 [285].

Raw material	kg/h
Wood	83333.33
Bark	14708.33
Chemicals	
Sulfuric acid	841.6667
Ammonia	516.6667
Cellulase	645.8333
CSL	1054.167
DAP	137.5
Natural gas	2333.333
Products	
Bioethanol	19129.17
Organosolv lignin	12937.5
Furfural	275
Acetic acid	1262.5
Biopower	3625

According to table of material balances in the study, all LCA inventory data are prepared and named as CS-3. Some parameters are missing, and one other study which was published by Bello et al. (2018) completed these parameters [118]. This study presented an LCA study based on Kautto’s work.

5.1.2.2 Functional unit

For LCA studies, two different functional unit approaches are adopted. First of all, to compare the impacts the process of IOBB such as organosolv pretreatment, furfural production, acetic acid recovery, enzyme production, saccharification and fermentation, distillation, wastewater treatment and cogeneration, 1 ton dry feedstock is selected as a functional unit. Therefore, each process impacts on the environment are presented individually.

5.1.2.3 Modeling approach

For selecting LCA study models, literature studies are taken as a reference, and according to the LCA studies of biorefineries, unit process based attributional LCA model is selected.

5.1.2.4 Allocation procedure

ISO 14040 series stated that allocation should be avoided, if possible [55, 56]. However, in IOBB, six products are producing at the same time. Thus, the allocation is not avoidable.

In the literature, different allocation procedures are used such as mass allocation, energy allocation, economic allocation, environmental burden effect allocation. The fundamental decision of selection of allocation procedure is its availability. Table 5.2 and Table 5.3 presents different allocation procedure approaches.

Mass allocation is applied according to flowrates. However, bioheat and biopower must be 0 because of not having weight. Thus, the mass allocation procedure is not suitable for IOBB. Economic allocation is suitable for IOBB. However, regional and

Table 5.2 : Energy content, economic value and fossil alternative GHG emissions for allocation calculations.

Product	Higher Heating Value	Economic Value	Fossil Alternative GHG Emissions
Bioethanol	27.4 MJ/kg	946.77 $/t [118]	92.2 g CO_{2eq}/MJ [406]
Organosolv lignin	24.7 MJ/kg	604.884 $/t [118]	355 g CO_{2eq}/kg [439]
Furfural	24.386 MJ/kg	986.442 $/t [118]	5780 g CO_{2eq}/kg [439]
Acetic acid	14.6 MJ/kg [440]	950.988 $/t [118]	2200 g CO_{2eq}/kg [439]
Bioheat	a	0.17 $/kW [60]	258 g CO_{2eq}/kW [406]
Biopower	a	0.02527814 $/kW [60]	643 g CO_{2eq}/kW [406]

[a]: Aspen Plus simulation outputs

Table 5.3 : Different allocation calculations for CS-1, CS-2 and CS-3.

Products	Quantity	Mass Allocation	Energy Allocation	Economic Allocation	Environmental Burden Effect Allocation
CS-1					
Bioethanol	1159.707 kg/h	0.46	0.38	0.44	0.42
Organosolv lignin	908.35 kg/h	0.36	0.30	0.22	0.05
Furfural	339.574 kg/h	0.13	0.11	0.12	0.29
Acetic acid	122 kg/h	0.05	0.04	0.01	0.04
Bioheat	7495.305 kW	0	0.12	0.19	0.11
Biopower	2139.134 kW	0	0.05	0.01	0.10
	Total	1	1	1	1
CS-2					
Bioethanol	1154.872 kg/h	0.45	0.38	0.45	0.42
Organosolv lignin	894.364 kg/h	0.35	0.30	0.22	0.05
Furfural	358.234 kg/h	0.14	0.12	0.14	0.30
Acetic acid	135 kg/h	0.05	0.04	0.01	0.04
Bioheat	7223.086 kW	0	0.11	0.17	0.10
Biopower	2063.738 kW	0	0.05	0.01	0.10
	Total	1	1	1	1
CS-3					
Bioethanol	459.1 MT/h	0.57	0.57	0.67	0.83
Organosolv lignin	310.5 MT/h	0.38	0.37	0.28	0.08
Furfural	6.6 MT/h	0.01	0.01	0.01	0.03
Acetic acid	30.3 MT/h	0.04	0.04	0.01	0.05
Bioheat	0	0	0.00	0	0
Biopower	3600 kW	0	0.01	0.03	0.01
	Total	1	1	1	1

seasonal changes in economic values are made economic allocation procedure variable. Fossil alternative environmental burden effect allocation method is also suitable for IOBB. However, energy based allocation procedure is selected because literature studies about LCA of biorefineries are generally used. As a result, energy based allocation procedure is decided to most suitable allocation procedure for IOBB. Therefore allocation is applied for the LCA studies according to Table 5.4.

Table 5.4 : Selected allocation procedure for CS-1 and CS-2.

Products	CS-1	CS-2	CS-3
Bioethanol	0.38	0.38	0.57
Organosolv lignin	0.30	0.30	0.37
Furfural	0.11	0.12	0.01
Acetic acid	0.04	0.04	0.04
Bioheat	0.12	0.11	0.00
Biopower	0.05	0.05	0.01

5.1.2.5 Impact assessment method and impact categories

The selection of impacts assessment method is made regarding literature studies about LCA of biorefineries. In general, ReCiPe (H) V1.04 is selected as midpoint and endpoint impact assessment method [118, 378, 380-384, 410] and ReCiPe (H) V1.04 is selected as endpoint impact assessment method [377, 385, 386]. Also, in some studies, the IPCC 2007 GWP method is used to determine GWP [376, 386, 411, 417]. Both three impact assessment methods are readily available in SimaPro LCA software. Therefore, any modification is not required. ReCiPe midpoint and endpoint impact assessment method is used in SimaPro LCA software in version V1.04. Hierarchist perspective (H) based on the most well-known policy principles and considers the time frame and other issues. ReCiPe impact assessment includes 18 indicators that presented in Table 5.5.

Table 5.5 : Midpoint impact assessment categories of ReCiPe V1.04 (H).

Impact Category	Abbreviation	Unit
Climate change	CC	kg $CO_{2\ eq}$
Ozone depletion	OD	kg CFC-11 $_{eq}$
Human toxicity	HT	kg 1,4-DB $_{eq}$
Photochemical oxidant formation	POF	kg NMVOC
Particulate matter formation	PMF	kg PM10 $_{eq}$
Ionizing radiation	IR	kg $U_{235\ eq}$
Terrestrial acidification	TA	kg $SO_{2\ eq}$
Freshwater eutrophication	FE	kg P $_{eq}$
Marine eutrophication	ME	kg N $_{eq}$
Terrestrial ecotoxicity	TEC	kg 1,4-DB $_{eq}$
Freshwater ecotoxicity	FEC	kg 1,4-DB $_{eq}$
Marine ecotoxicity	MEC	kg 1,4-DB $_{eq}$
Agricultural land occupation	ALO	m^2a
Urban land occupation	ULO	m^2a
Natural land transformation	NLT	m^2
Water depletion	WD	m^3
Metal depletion	MD	kg Fe $_{eq}$
Fossil depletion	FD	kg oil $_{eq}$

In Table 5.5, CFC-11 is trichlorofluoromethane, DB is dichlorobenzene, NMVOC is a non-methane volatile organic compound, PM is particulate matter, and a is the year.

Normalization factors of midpoint characterization for ReCiPe V1.04 (H) method is given in Table 5.6.

Table 5.6 : Normalization factors used in ReCiPe impact category (World, 2000).

Impact category	Unit	Normalization Factor
CC	1 / kg $CO_{2eq.}$	2.63E-01
OD	1 / kg CFC-$11_{eq.}$	7.51E-10
HT	1 / kg 1,4-$DB_{eq.}$	1.68E-01
POF	1 / kg NMVOC	1.95E-01
PMF	1 / kg $PM10_{eq.}$	1.45E-01
IR	1 / kg $U_{235eq.}$	2.79E-02
TA	1 / kg $SO_{2eq.}$	1.09E+00
FE	1 / kg $P_{eq.}$	3.09E-04
ME	1 / kg $N_{eq.}$	2.69E-01
TEC	1 / kg 1,4-$DB_{eq.}$	2.16E-02
FEC	1 / kg 1,4-$DB_{eq.}$	7.69E-03
MEC	1 / kg 1,4-$DB_{eq.}$	7.67E-03
ALO	1 / m^2a	4.91E+01
ULO	1 / m^2a	3.50E-02
NLT	1 / m^2	1.45E-04
WD	1 / m^3	0.00E+00
MD	1 / kg $Fe_{eq.}$	1.33E-04
FD	1 / kg $oil_{eq.}$	1.72E-01

ReCiPe V1.04 (H) hierarchist endpoint impact assessment method is used to determine endpoint categories and damage assessment. 11 characterization impact categories and three damage assessment categories are found in the ReCiPe impact assessment method that presented in Table 5.7. In Table 5.7, DALY indicates disability-adjusted life years and PDF presents potentially disappeared fraction of species. The characterization factors carcinogens, respiratory organics, respiratory inorganics, climate change, radiation and ozone layer are merged and generate the damage assessment category, human health. Ecotoxicity, acidification/eutrophication, and land use compose ecosystem quality and minerals, and fossil fuel generates resources damage assessment.

Table 5.7 : Characterization and damage assessment categories and units of ReCiPe.

Characterization	Unit	Damage Assessment	Unit
Carcinogens	DALY	Human Health	DALY
Respiratory organics	DALY		
Respiratory inorganics	DALY		
Climate change	DALY		
Radiation	DALY		
Ozone layer	DALY		
Ecotoxicity	PDF*m^2yr	Ecosystem Quality	PDF*m^2yr
Acidification/ Eutrophication	PDF*m^2yr		
Land use	PDF*m^2yr		
Minerals	MJ surplus	Resources	MJ surplus
Fossil fuels	MJ surplus		

5.2 Inventory Analysis of the LCA study

In this section, inventory data for LCA study is presented. Through the goal and scope definition, inventory data is prepared. The subtitles in this section are:

- Data sources and data usage
- General data and assumptions for LCA inventory
- LCA inventory based on feedstock

5.2.1 Data sources and data usage

The data of the LCA study is prepared based on Aspen Plus simulation software input and outputs which presented in Chapter 3. While commercial IOBB which produce the designed products is not found in Turkey and the world. Therefore, experimental studies are based on developing design and simulation. To determine the LCA study, both Aspen Plus simulation software and Simapro LCA software conduct together. However, some data are missing or should be making assumptions. Other literature studies and the Ecoinvent database are examined to fill missing data. All assumptions are made and present as clear and detailed as possible in the study.

The Ecoinvent database includes several libraries such as Ecoinvent system processes, Ecoinvent unit processes, LCA Food DK, etc. According to literature studies, Ecoinvent unit processes library is selected and applied. The regional explanations are specified in the Ecoinvent database. GLO is used as global datasets, RER means Regional such as European, and ROW means Rest of World.

5.2.2 General data and assumptions for LCA inventory

The data which are used in LCA inventory is obtained from Aspen Plus simulation software, literature studies, SimaPro Databases, and assumptions. This section is configurated to explain how LCA inventory data are selected, assumed or calculated.

- Mass and energy balances for each material are calculated by Aspen Plus simulation software which was described in Chapter 3.
- IOBB is found self-sufficient biorefinery, considering heat and work balances. The heat and work requirements are supplied by bioheat and biopower which are produced in the cogeneration process. In each process, 10% of heat is assumed to be lost during to process.

- According to literature studies and current commercial biorefineries, the technical, operational lifetime of IOBB is selected as 20 years.
- The annual operational working hour is selected as 8000 hours. IOBB is assumed to work continuously, except one-month shut-down for maintenance and vacations. The operational performance actors are presented in Table 5.8. In Table 5.8, the availability factor is calculated as annual operational hours divided by annual full load hours. The capacity factor is calculated by the multiplication of the availability factor and load factor.

Table 5.8 : The operational performance factors of IOBB.

	Unit	Value
Technical lifetime	A	20
Annual operational working hours	h/a	8000
Availability factor	%	91.3
Load factor	%	85
Capacity factor	%	77.63

- The dry matter loss is assumed as 5% during transportation because of having small dimensions. Therefore, 5.775 kg/h of SOC (5250 kg/h of wood and 525 kg/h of bark) is required for CS-1, 5.1975 kg/h of SOC (4725 kg/h of wood and 472.5 kg/h of bark) and 525 kg/h of IWS are required for CS-2, respectively.
- For transportation of chemicals, chemicals which are bought from the seller are selected as cellulose, CSL, NH_3, SO_2, DAP, WNUTR, Biomass, H_2SO_4, oil, CNUTR, and undecane.
- The woody feedstock for all cases is assumed to have chips or dust dimensions. Therefore, chipping and grinding are not required.
- The lower heating value of bioethanol is accepted as 27.4 MJ/kg, and all data reductions are based on the LHV of bioethanol [285].
- When considering literature studies, energy based allocation procedure is found more acceptable and applicable for IOBBs. Also, the calculation of the allocation procedure is presented in Table 5.9.

5.2.3 Feedstock based LCA inventory

The LCA inventory data per 1 ton (1000 kg) of the dry feedstock of IOBB utilizing SOC and industrial wood sawdust are presented in this chapter. For determining the

Table 5.9 : The process products, requirements, emissions and wastes of IOBB.

IOBB	Unit	Case 1	Case 2	Case 3
Annual production				
Ethanol	t/a	9277.656	9238.976	153033
Organosolv lignin	t/a	7266.8	7154.912	103500
Furfural	t/a	2716.592	2865.872	2200
Acetic acid	t/a	976	1080	10100
Biopower	GWh/a	59962.44	57784.69	29000
Bioheat	GWh/a	17113.08	16509.91	na
Annual Feedstock Requirements				
Wood (dry)	t/a	40000	40000	666667
Air	t/a	159658.504	159658.48	
Bark	t/a	4000	3600	117667
Cellulase	t/a	422.256	312.832	5166.667
CNUTR	t/a	81.6	81.6	
CSL	t/a	340.856	338.064	8433.333
DAP	t/a	10.64	10.568	1100
Ethanol	t/a	370.64	364.48	
H_2SO_4	t/a	510	510	6733.33
NH_3	t/a	35.904	35.904	4133.333
Oil	t/a	97.104	97.104	
SO_2	t/a	35.904	35.904	
Undecane	t/a	0.144	0.12	
WNUTR	t/a	60.44	60.44	
Bioheat	GWh/a	40.149289	40.403098	
Biopower	GWh/a	8.5398	8.557	
Water	t/a	171201.6	172359.8	

impacts of IOBB plants, each process is examined individually. To comparison of transportation, organosolv pretreatment, furfural production, acetic acid recovery, enzyme production, saccharification and fermentation, distillation, wastewater treatment, and cogeneration are made according to feedstock based functional unit.

5.2.3.1 LCA inventory for feedstock transportation

Feedstock transportation includes wood transportation from forest to IOBB, industrial wood sawdust transportation from manufacturer to IOBB and chemical transportation from market to IOBB. Table 5.10 presents the LCI data for feedstock transportation.

As it is seen in Table 5.10, the unit of feedstock transportation is ton.kilometer which is abbreviated as tkm. It is calculated by multiplication of total mass (ton) and distance (km). In CS-1, only SOC is used as feedstock and IOBB is assumed to located 50 km distance from forest. In CS-2, both SOC and IWS are used, and IWS manufacturers are 15 km away from IOBB. Both CS-1 and CS-2, chemicals are assumed to buy 45 km away from IOBB. An article about CS-3 stated that transportation of all chemicals and feedstocks are 100 km away from biorefinery [118]. In both 3 cases, 5% of wood feedstock is assumed to be lost during transportation. The vehicle properties are selected as “Transport, lorry, 16-32 t, EURO5/RER U” in SimaPro software for all cases. The woody feedstock for all cases is assumed to have chips or dust dimensions. Therefore, chipping and grinding are not required.

Table 5.10 : LCI data for feedstock transportation.

Input	Unit	Case 1	Case 2	Case 3
Transportation of SOC	tkm	50	50	105
Transportation of IWS	tkm	0	15	0
Transportation of chemicals	tkm	76.0025981	89.3776254	4.028361345
Total	tkm	126.0025981	154.3776254	109.0283613

5.2.3.2 LCA inventory for organosolv pretreatment

At organosolv pretreatment process, wood, water, sulfuric acid, ethanol, natural gas, bioheat, and biopower are required. The outputs are defined as organosolv lignin and heat. Table 5.11 shows the required LCI data for organosolv pretreatment. Wood and water are classified in inputs from nature as seen in Table 5.11. Woods are selected as “Wood chips, softwood, u=140%, at forest/RER U” to define SOC samples for CS-1, “Wood chips, softwood, u=140%, at forest/RER U” and “Wood chips, mixed, from industry, u=40%, at plant/RER U” to define SOC and IWS samples for CS-2 and

Table 5.11 : LCI data for organosolv pretreatment.

	Unit	Case 1	Case 2	Case 3
Input from technosphere				
Wood	kg	1000	1000	1000
Water	kg	3907.675	3937.176	4800.648
H_2SO_4	kg	12.74678	12.74859	9.80677
Ethanol	kg	0	0	4.903385
Natural gas	kg	0	0	5.253626
Biopower	kW	34.50111	34.57549	780.3123
Heat	MJ	0	0	1970.789
Outputs to technosphere				
Organosolv lignin	kg	181.6241	178.853	152.8222
Heat				
Outputs to the environment				
Waste heat	MJ	2.4236	2.428892	0

"Wood chips, hardwood, u=140%, at forest/RER U" to define hybrid poplar sample in CS-3. Water is selected as "Tap water". Inputs from the technosphere section include materials, fuels, electricity and heat requirements for production. Sulfuric acid is selected as "sulfuric acid, liquid, at plant/RER U", bioethanol is defined as "Ethanol, 99.7% in H_2O, from biomass, production RER, at service station/CH U", natural gas is selected as "Natural gas, high pressure, at customer/RER U". "Electricity, wood, at distillery/CH U" is selected for all biopower and "Heat, unspecific, in chemical plant/RER U" is selected for all heats. Waste heat selection is made with "Heat, waste". According to design differences between IOBB simulation and CS-3, input parameters differ. In IOBB, make-up ethanol is supplied from IOBB own bioethanol production, whereas in CS-3 the fossil based ethanol is purchased. Additionally, natural gas is required for lignin drying in CS-3, while biopower is used for lignin drying in CS-1 and CS-2.

5.2.3.3 LCA inventory for furfural production

Furfural production process includes both solvent recovery and furfural production processes. Therefore, these separate processes are merged to create LCI data tor furfural production in CS-3. Table 5.12 presents the LCI data for furfural production.

As it is seen in Table 5.12, sulfuric acid is not required for CS-3 because of furfural recovery is designed in CS-3, instead of furfural production. Therefore, only solvent recovery and furfural separation are found in the furfural production process in CS-3. In IOBB, sulfuric acid is required for xylose to furfural conversion. As a conclusion,

Table 5.12 : LCI data for furfural production.

	Unit	Case 1	Case 2	Case 3
Input from technosphere				
H_2SO_4	kg	19.89497	19.99778	0
Heat	MJ	49.71269	49.94166	28.01935
Biopower	kW	37.15504	37.23515	44.34973
Outputs to technosphere				
Furfural	kg	67.98283	71.59207	3.268923
Outputs to the environment				
Waste heat	MJ	5.272788793	5.30348658	0

furfural is defined as product and sulfuric acid, heat and biopower are defined as inputs for furfural production. Sulfuric acid, heat, and biopower are defined as described in the organosolv pretreatment section.

5.2.3.4 LCA inventory for acetic acid recovery

Acetic acid recovery process includes extraction and distillation steps for acetic acid recovery. Therefore, the required chemical consists of only make-up undecane. The Ecoinvent database does not contain undecane. Therefore heptane is selected in order to undecane. Table 5.13 includes LCI data for acetic recovery for CS-1,-2 and -3.

Table 5.13 : LCI data for acetic acid recovery.

	Unit	Case 1	Case 2	Case 3
Input from technosphere				
Undecane	kg	1.166263891	0.627850875	0.933979865
Heat	MJ	53.11798773	54.46739914	46.25527171
Biopower	kW	15.39280363	15.42599292	18.37345884
Outputs to technosphere				
Acetic acid	kg	24.39383815	26.99700574	15.17714511
Outputs to the environment				
Waste heat	MJ	0.060133103	0.07015151	0

The Ecoinvent database does not contain undecane. Therefore heptane is selected in order to undecane and selected as “Chemicals, inorganic, at plant/RER U”. The other inputs heat and biopower are defined above. Acetic acid defined as the product of acetic acid recovery process.

5.2.3.5 LCA inventory for enzyme production

Enzyme production process requires some chemicals and release exhaust gases. The article that contains CS-3 data does not include the enzyme production part. However, it contains only input and output main streams. Therefore, some data are missing in CS-3. Existed data are used. Table 5.14 indicates the LCI data for enzyme production.

Table 5.14 : LCI data for enzyme production.

	Unit	Case 1	Case 2	Case 3
Input from technosphere				
NH_3	kg	0.897370886	0.897498427	3.035431485
SO_2	kg	0.897370886	0.897498427	3.035431485
CSL	kg	4.77499226	4.723273575	2.101451619
Nutrients	kg	2.039485502	2.039772529	2.480895172
Oil	kg	2.426986566	2.427329371	0
Heat	MJ	0	0	37.91365707
Biopower	kW	12.03943597	12.06539246	14.37074602
Outputs to technosphere				
Heat	MJ	32.62815651	35.70504135	0
Outputs to the environment				
Waste heat	MJ	0.015630517	0.017176103	0
H_2O	kg	0.408896638	0.413154201	0.350242142
Ethanol	kg	0	0	0.350242142
Furfural	kg	0.000399899	0.000399956	0
CO_2	kg	2.433183947	2.746894003	19.96378731
O_2	kg	2.885468471	2.661705655	0.116747175
NH_3	kg	0.287327262	0.28036883	0
Acetic acid	kg	0.001999498	0.001999778	0
SO_2	kg	0.650836939	0.64933057	0

Air is the only input from nature for enzyme production. “Ammonia, liquid, at regional storehouse/RER U” is defined for ammonia, “Sulfur dioxide, liquid, at plant/RER U” is defined for sulfur dioxide, “Syrup, from sugar beet molasses, at distillery/CH U” is defined for CSL, “Proteins, from grass, at digestion/CH U” is defined for nutrients, “Corn oil, at regional storage/CH U” is defined as oil. Heat and biopower are described in previous sections. All exhaust gases are found in the Ecoinvent database and selected in the database. Therefore, any modification is required for exhaust gases.

5.2.3.6 LCA inventory for saccharification and fermentation

For the saccharification and fermentation process, all data are available in both CS-1, CS-2, and CS-3. LCI data for saccharification and fermentation process are presented in Table 5.15.

All inputs except cellulase are defined in the previous section such as water, CSL, heat, and biopower. “Diammonium phosphate, as N, at regional storehouse/RER U” is defined for DAP and “Yeast paste, from whey, at fermentation/CH U” is defined for cellulase.

Table 5.15 : LCI data for saccharification and fermentation.

	Unit	Case 1	Case 2	Case 3
Input from technosphere				
Water	kg	82.86026402	82.87761538	132.5081641
Cellulase	kg	10.55353141	7.820131858	7.588575634
CSL	kg	3.744256462	3.727389477	0.933979865
DAP	kg	2.654244605	2.643178644	1.400969798
Heat	MJ	0	0	38.71216622
Biopower	kW	3.849288712	3.857592333	4.594667906
Outputs to technosphere				
Heat	MJ	165.294239	164.8245348	0
Outputs to the environment				
Waste heat	MJ	0.079183879	0.079289437	0

5.2.3.7 LCA inventory for distillation

In the bioethanol distillation process, air, water, and biopower are required for distillation and ethanol, and exhaust gases are outputs. Detailed LCI data for distillation process is shown in Table 5.16.

Table 5.16 : LCI data for distillation.

	Unit	Case 1	Case 2	Case 3
Input from technosphere				
Water	kg	288.2271816	288.2680527	204.0742436
Biopower	kW	7.585147318	7.601503225	9.053932794
Outputs to technosphere				
Bioethanol	kg	231.941401	230.974401	223.3278128
Heat	MJ	409.6179086	410.0491537	0
Outputs to the environment				
Waste heat	MJ	2.349306621	2.36108528	0
Ethanol	kg	1.469829908	1.469235919	0.933979865
H_2O	kg	8.022171489	8.014111458	0.350242142
CO_2	kg	211.9688444	211.5611514	7.121585702
O_2	kg	2.344406614	2.366740536	0
NH_3	kg	0.030992191	0.030396616	0
Lactic acid	kg	0.000199950	0.000199978	0
Acetic acid	kg	0.001199700	0.001199867	0
SO_2	kg	0.090576874	0.090789782	0

All input from nature and technosphere are defined in previous sections. The vapor fraction contents are found directly in the Ecoinvent database. Therefore, any assumption or modification are required for selecting data. The main difference between CS-1, CS-2, and CS-3, the exhaust gases are not well defined in CS-3. Only major components are given in output streams. It is assumed that only ethanol, water, and carbon dioxide are found in output vapor stream in CS-3, while nitrogen, oxygen, ammonia, lactic acid, acetic acid, and sulfur dioxide are also found in vapor stream in CS-1 and CS-2. Additionally, due to design differences, the results are not similar for IOBB and CS-3.

5.2.3.8 LCA inventory for wastewater treatment

Wastewater treatment is one of the main difference between IOBB and CS-3. Wastewater design and simulation are excluded in CS-3. Therefore, the CS-3 results are produced from wastewater and other waste liquid streams. Table 5.17 presents the wastewater treatment process data for LCI.

The detailed stream results are presented in Table 5.17. Nutrients are defined as “Chemicals organic, at plant/GLO U” from the Ecoinvent database. Biopower and heat are described, previously. Due to the Ecoinvent database wastewater content, some assumptions are required. Glucose, xylose, arabinose, galactose, mannose, glucooligomers, cellobiose, CSL, and nutrients are defined as “Hydrocarbons, unspecified”, 5-HMF and furfural described as “Furfural”, extractives, carbon dioxide, oxygen, nitrogen oxide, DAP, hydrogen sulfide are described as “Solved substances, inorganic” and levulinic acid and succinic acid are described as “Acids, unspecified”. The other outputs are found directly in the Ecoinvent database.

5.2.3.9 LCA inventory for cogeneration

Cogeneration process is the most complicated part in IOBB due to having lots of emissions both vapor and solid. In IOBB, only solid wastes and bark are combusted in boiler, solid wastes, bark and natural gas are used for combustion in CS-3. The products of the cogeneration process are bioheat and biopower for IOBB, and only biopower for CS-3. Especially exhaust gas stream, only significant components such as water and carbon dioxide is defined in CS-3. Minor components are not defined. Therefore, these missing data could be effects the LCA results. However, any modifications or assumption are made for missing data. LCA inventory data for the cogeneration process is presented in Table 5.18.

Table 5.17 : LCI data for wastewater treatment.

	Unit	Case 1	Case 2	Case 3
Input from technosphere				
Nutrients	kg	1.510619494	1.510833485	0
Biopower	kW	72.37777562	72.53382979	86.39298367
Outputs to technosphere				
Heat	MJ	5638.465844	5584.325063	0
Outputs to the environment				
Waste heat	MJ	2.7010969	2.0553027	0
Outputs to the environment				
Glucose	kg	0.0011997	0.001199867	6.537846747
Xylose	kg	0.001399645	0.001399845	6.421097726
HMF	kg	0.007198162	0.006799221	0.583736493
Arabinose	kg	0.003799038	0.003599601	0.116747175
Galactose	kg	0.0011997	0.002799689	14.00967336
Mannose	kg	0.001799547	0.001599823	14.00967336
Glucooligomers	kg	0.019994978	0.019597839	18.56281751
Cellobiose	kg	0.005998487	0.005799357	0
Xylitol	kg	0.001399645	0.001399845	0
Extractives	kg	0.066983313	0.062793135	0
Ethanol	kg	0.002799296	0.002799689	0.817230843
H_2O	kg	3458.940097	3489.293263	3290.522041
Furfural	kg	0.002399394	0.002599712	1.284220776
H_2SO_4	kg	8.095551718	7.854530321	0
N_2	kg	0.053186586	0.053594068	0
CO_2	kg	0.012596846	0.012598615	0
O_2	kg	0.027593017	0.027796892	0
NO_2	kg	0.055186034	0.051794231	0
NH_3	kg	1.090521571	1.009285694	0
Lactic acid	kg	0.086578102	0.086390468	0
Acetic acid	kg	0.063184075	0.064993101	1.517712665
Glycerol	kg	0.006598315	0.006399278	0
Succinic acid	kg	0.011197183	0.01099878	0
DAP	kg	0.129567541	0.127985557	13.89292434
Oil	kg	0.023394089	22.79747151	80.67236776
CSL	kg	0.070582394	0.069992237	0
Wnutrients	kg	1.5068215	1.507032755	0
SO_2	kg	0.051986893	0.052194236	0
H_2S	kg	0.002799296	0.002399734	0
Levulinic acid	kg	0.005798536	0.005399401	0
Formic acid	kg	0.000599849	0.000599933	0.116747175
Soluble ash	kg	0.004598836	0.006999224	0

All inputs from nature and technosphere and outputs to technosphere and environment (vapor) components are described in previous sections. Therefore solid waste is not defined. Cellulose, xylan, lignin, cellulose, biomass, ZYMO, arabinan, mannan, and galactan are described as “Hydrocarbons” in emission to soil section. Tar, acetate, and ash are selected directly from the Ecoinvent database.

Table 5.18 : LCI data for cogeneration process.

	Unit	Case 1	Case 2	Case 3
Input from nature				
Water	kg	0	0	658.337905
Bark	kg	99.98607804	89.99992332	116.5465419
Air	kg	2714.532185	2616.5506	0
Input from technosphere				
Natural gas	kg	0	0	21.9484899
Biopower	kW	15.64924593	15.68298788	19.41516538
Outputs to technosphere				
Heat	MJ	5389.258004	5239.909037	0
Electricity	kW	219.6397108	207.3522206	375.297208
Outputs to the environment - vapor				
H_2O	kg	1.101523943	1.080082027	108.8792145
N_2	kg	3212.944247	3114.820768	0
CO_2	kg	723.1562962	698.0674291	684.2464578
O_2	kg	351.6383595	394.8056391	0
CH_4	kg	0.080379478	0.080790891	0
NO	kg	0.785799372	1.351648515	0
NO_2	kg	0.022994212	0.02199756	0
Lactic acid	kg	0.0011997	0.001199867	0
Acetic acid	kg	0.00019995	0.033596286	0
SO_2	kg	3.293370544	3.394621333	0
H_2S	kg	0.068183006	0.13538522	0
CO	kg	0.000599849	0.000599933	0
Levulinic acid	kg	0.000599849	0.000599933	0
Formic acid	kg	0.003799038	0.000399956	0
Outputs to the environment - solid				
Cellulose	kg	0.185953145	0.18057986	0.350242142
Xylan	kg	0.297524659	0.313965054	0.116747175
Lignin	kg	0.635638747	0.625931939	1.167471754
Cellulase	kg	0.097175189	0.072792026	0
Biomass	kg	0.024593783	0.024597284	0.116747175
ZYMO	kg	0.07618055	0.076191636	0
Acetate	kg	0.057385514	0.064592601	0.116747175
Arabinan	kg	0.125368613	0.114587056	0
Mannan	kg	0.275330325	0.25157242	0
Galactan	kg	0.000799798	0.0017998	0
Tar	kg	0.130366922	0.136784804	0.583736493
Ash	kg	4.693102288	7.080252302	0

6. LIFE CYCLE ASSESSMENT OF INTEGRATED ORGANOSOLV BASED BIOREFINERY RESULTS AND DISCUSSIONS

This chapter presents the results of LCA study via SimaPro software for case studies. The goal and scope definition, methodology selection, assumptions and inventory analysis which are used in SimaPro LCA software for LCA study are defined in Chapter 4, and the SimaPro software results are described in this section**.**

The results include midpoint impacts and endpoint impacts. For defining midpoint impacts, ReCiPe Midpoint (H) V1.04 method is selected. The results are given as the impacts on CC, OD, HT, POF, PMF, IR, TA, FE, ME, TEC, FEC, MEC, ALO, ULO, NLT, WD, MD and FD. For defining endpoint effects, ReCiPe Endpoint 99 (H) V1.04 method is selected, and it is used to determine damage assessment to present impacts on human health (HH), ecosystem quality (EQ) and resources.

Functional unit results declare how many environmental impacts occur when 1 ton dry feedstock is consumed. First of all, analyzing each case study is presented. Next, comparison of Case Studies is defined. Feedstock based functional unit provides to compare each production step in IOBB. The abbreviation of process names in the LCA study is listed in Table 6.1.

Table 6.1 : Abbreviations of IOBB process in LCA studies.

IOBB Units	CS-1	CS-2	CS-3
Transportation of Feedstock	C1T	C2T	C3T
Organosolv Pretreatment	C1O	C2O	C3O
Furfural Production	C1F	C2F	C3F
Acetic Acid Recovery	C1A	C2A	C3A
Enzyme Production	C1E	C2E	C3E
Saccharification and Fermentation	C1S	C2S	C3S
Distillation	C1D	C2D	C3D
Wastewater Treatment	C1W	C2W	C3W
Cogeneration	C1C	C2C	C3C

6.1 Analysis of CS-1

Analysis of CS-1 presents the midpoint impact categories, normalization, damage assessment, weighting and single score. Midpoint characterization results of CS-1 are presented in Figure 6.1 and Table 6.2.

In CS-1, total CC is found as 45.5943 $kgCO_{2eq}$. The most contributions are revealed from organosolv pretreatment (15.17882 $kgCO_{2eq}$), enzyme production (10.19287 $kgCO_{2eq}$), acetic acid production (7.252313 $kgCO_{2eq}$) and furfural production (6.604575 $kgCO_{2eq}$). Other processes such as transportation, saccharification and fermentation, distillation, wastewater treatment and cogeneration are lower than 3 $kgCO_{2eq}$. At OD category, total OD result are found as 5.85E-06 kgCFC-11_{eq}. Organosolv pretreatment, enzyme production, saccharification and fermentation and furfural production increase the OD results. Organosolv pretreatment has also the most contribution at MEC (0.031916 kg1,4-DB_{eq}), ALO (509.8962 m^2a), ULO (5.07608 m^2a), NLT (0.042581 m^2), WD (5.10466 m^3), MD (0.212712 $kgFe_{eq}$), and FD (5.516837 $kgoil_{eq}$). Total HT results are found as 4.190301 kg1,4-DB_{eq}. The important result in this category is saccharification and fermentation process has negative result. This means it has a positive contribution on environment. In addition, saccharification and fermentation process has negative results at FE (-9.2E-05 kgP_{eq}), TEC (-8.4E-05 kg1,4-DB_{eq}), FEC (-0.00072 kg1,4-DB_{eq}), MEC (-0.00332 kg1,4-DB_{eq}) and NLT (-2.8E-05 m^2) categories. Total POF result is 2.565918 kgNMVOC. 1.08076 kgNMVOC and 0.998367 kgNMVOC are formed by cogeneration and distillation processes. On the other hand, cogeneration has the most contributions at PMF (0.837219 $kgPM10_{eq}$) and TA (3.747564 $kgSO_{2\ eq}$)categories. Wastewater treatment has the most impact at ME (0.90034 kgN_{eq}) category. At TEC and FEC categories, enzyme production has the highest impact with the result of 0.368471 kg1,4-DB_{eq} and 0.090797 kg1,4-DB_{eq}, respectively. At all categories, the lowest impacts are formed by transportation.

In midpoint characterization categories, all units are different and comparing the results are complicated. Therefore, normalization is required to make easy comparison. The normalization factors that used in ReCiPe V1.04 (H) were explained in previous section in Table 5.6. Midpoint normalization results are shown in Figure 6.2 and Table 6.3. Endpoint weighting results are given in Figure 6.3 and Table 6.4.

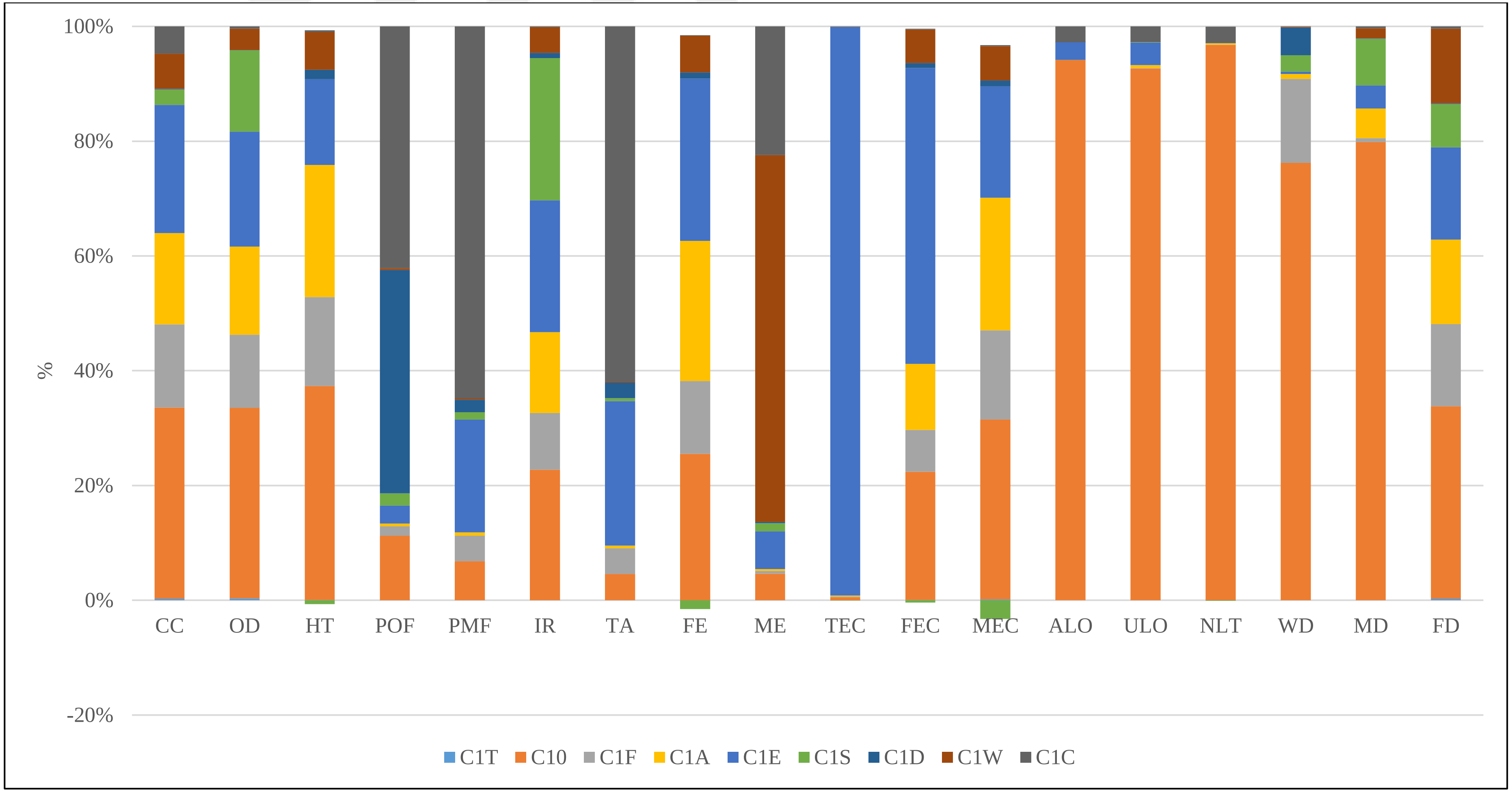


Figure 6.1 : Midpoint characterization results of CS-1.

Table 6.2 : Midpoint characterization results of CS-1.

Impact Category	Unit	Total	C1T	C10	C1F	C1A	C1E	C1S	C1D	C1W	C1C
CC	kg CO_{2eq}	45.5943	0.136514	15.17882	6.604575	7.252313	10.19287	1.213671	0.069108	2.770895	2.175537
OD	kg CFC-11$_{eq}$	5.85E-06	2.05E-08	1.94E-06	7.46E-07	8.97E-07	1.17E-06	8.29E-07	3.42E-09	2.17E-07	2.31E-08
HT	kg 1,4-DB$_{eq}$	4.190301	0.002549	1.584355	0.656331	0.978045	0.636102	-0.02839	0.068869	0.277863	0.014575
POF	kg NMVOC	2.565918	0.00054	0.287589	0.041974	0.012995	0.080919	0.054113	0.998367	0.008661	1.08076
PMF	kg PM10$_{eq}$	1.291309	0.000148	0.087649	0.057384	0.007581	0.253849	0.016754	0.028124	0.002601	0.837219
IR	kg U_{235eq}	5.913878	0.001621	1.343854	0.583627	0.8337	1.358088	1.467291	0.053502	0.263669	0.008525
TA	kg SO_{2eq}	6.052871	0.000365	0.276135	0.272109	0.02689	1.526035	0.028873	0.1668	0.008099	3.747564
FE	kg P_{eq}	0.005797	1.68E-06	0.001524	0.000759	0.00146	0.001691	-9.2E-05	6.65E-05	0.000382	4.75E-06
ME	kg N_{eq}	1.407827	0.000177	0.064877	0.007443	0.004016	0.092808	0.019885	0.002909	0.90034	0.315371
TEC	kg 1,4-DB$_{eq}$	0.371787	1.83E-05	0.001899	0.000503	0.000621	0.368471	-8.4E-05	0.000135	0.000172	5.2E-05
FEC	kg 1,4-DB$_{eq}$	0.174731	8.9E-05	0.039323	0.012915	0.020284	0.090797	-0.00072	0.001512	0.010328	0.0002
MEC	kg 1,4-DB$_{eq}$	0.095235	0.000159	0.031916	0.015849	0.023558	0.019754	-0.00332	0.001038	0.006115	0.000165
ALO	m^2a	541.5526	6.72E-06	509.8962	0.00187	0.00989	16.65181	0.078846	0.005394	0.001334	14.90729
ULO	m^2a	5.479088	4.93E-06	5.07608	0.005177	0.027752	0.217389	0.003299	0.000207	0.000881	0.148298
NLT	m^2	0.043927	2.52E-08	0.042581	1.99E-05	9.61E-05	1.03E-05	-2.8E-05	1.4E-06	3.22E-06	0.001244
WD	m^3	6.698682	0.000123	5.10466	0.981692	0.05607	0.029413	0.188943	0.325902	0.010378	0.0015
MD	kg Fe_{eq}	0.266393	5.84E-06	0.212712	0.00176	0.013844	0.010671	0.021646	0.000158	0.004733	0.000864
FD	kg oil$_{eq}$	16.44724	0.046002	5.516837	2.353431	2.419888	2.649303	1.236485	0.019687	2.142587	0.06302

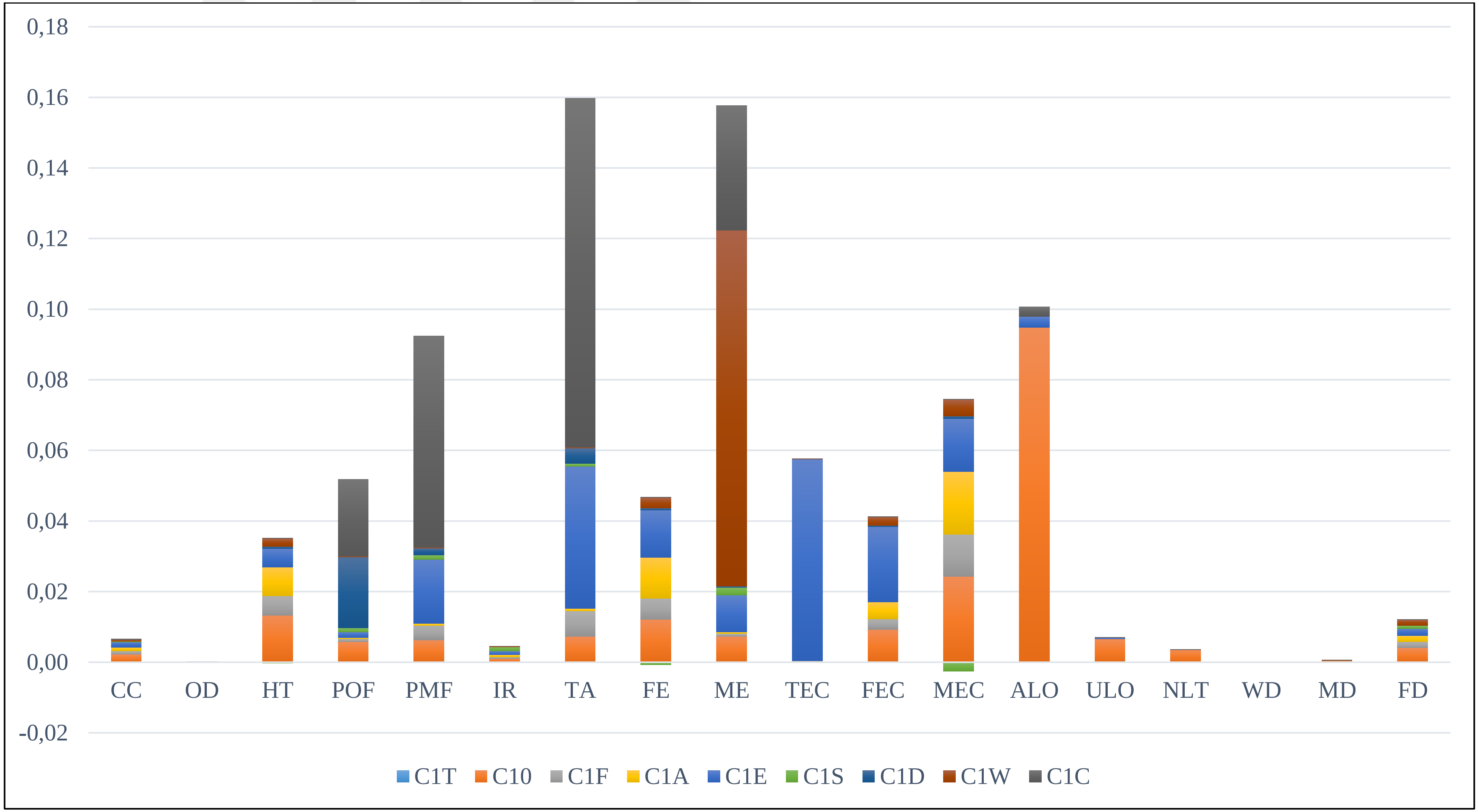


Figure 6.2 : Normalization of midpoint results of CS-1.

Table 6.3 : Normalization of midpoint results of CS-1.

Impact Category	Total	C1T	C10	C1F	C1A	C1E	C1S	C1D	C1W	C1C
CC	0.006657	1.99E-05	0.002216	0.000964	0.001059	0.001488	0.000177	1.01E-05	0.000405	0.000318
OD	0.000157	5.5E-07	5.2E-05	2E-05	2.4E-05	3.15E-05	2.22E-05	9.16E-08	5.82E-06	6.2E-07
HT	0.034989	2.13E-05	0.013229	0.00548	0.008167	0.005311	-0.00024	0.000575	0.00232	0.000122
POF	0.051832	1.09E-05	0.005809	0.000848	0.000263	0.001635	0.001093	0.020167	0.000175	0.021831
PMF	0.092458	1.06E-05	0.006276	0.004109	0.000543	0.018176	0.0012	0.002014	0.000186	0.059945
IR	0.00453	1.24E-06	0.001029	0.000447	0.000639	0.00104	0.001124	4.1E-05	0.000202	6.53E-06
TA	0.159796	9.64E-06	0.00729	0.007184	0.00071	0.040287	0.000762	0.004404	0.000214	0.098936
FE	0.045973	1.33E-05	0.012088	0.006019	0.01158	0.013407	-0.00073	0.000527	0.00303	3.77E-05
ME	0.157677	1.99E-05	0.007266	0.000834	0.00045	0.010395	0.002227	0.000326	0.100838	0.035322
TEC	0.057627	2.83E-06	0.000294	7.8E-05	9.62E-05	0.057113	-1.3E-05	2.09E-05	2.67E-05	8.07E-06
FEC	0.041062	2.09E-05	0.009241	0.003035	0.004767	0.021337	-0.00017	0.000355	0.002427	4.71E-05
MEC	0.071998	0.00012	0.024128	0.011982	0.01781	0.014934	-0.00251	0.000785	0.004623	0.000125
ALO	0.100729	1.25E-09	0.094841	3.48E-07	1.84E-06	0.003097	1.47E-05	1E-06	2.48E-07	0.002773
ULO	0.007123	6.41E-09	0.006599	6.73E-06	3.61E-05	0.000283	4.29E-06	2.69E-07	1.14E-06	0.000193
NLT	0.003677	2.11E-09	0.003564	1.66E-06	8.04E-06	8.63E-07	-2.4E-06	1.17E-07	2.7E-07	0.000104
WD	0	0	0	0	0	0	0	0	0	0
MD	0.000602	1.32E-08	0.000481	3.98E-06	3.13E-05	2.41E-05	4.89E-05	3.57E-07	1.07E-05	1.95E-06
FD	0.012056	3.37E-05	0.004044	0.001725	0.001774	0.001942	0.000906	1.44E-05	0.001571	4.62E-05

Table 6.4 : Weighting of endpoint results of CS-1.

Damage Category	Unit	Total	C1T	C10	C1F	C1A	C1E	C1S	C1D	C1W	C1C
Total	Pt	15.8185	0.015795	5.035923	1.094748	0.847655	2.596551	0.413277	0.172867	0.588173	5.053582
Human Health	Pt	9.01286	0.005181	1.0113013	0.5514153	0.2870251	1.8070157	0.1357714	0.1677871	0.1064204	4.940948
Ecosystems	Pt	3.18762	0.000508	2.8124189	0.0253821	0.027805	0.2061236	0.0055025	0.0007499	0.0103408	0.0987895
Resources	Pt	3.61808	0.010105	1.2122035	0.5179512	0.5328248	0.5834120	0.2720035	0.0043301	0.4714123	0.0138445

According to normalization results, the maximum impact is formed at TA category (0.159796). It is followed by ME (0.157677), ALO (0.100729), PMF (0.092458), MEC (0.071998), TEC (0.057627), POF (0.051832), FE (0.045973), FEC (0.041062), HT (0.034989), FD (0.012056), ULO (0.007123), CC (0.006657), IR (0.00453), NLT (0.003677), MD (0.000602), OD (0.000157), and WD. The process contributions are similar to midpoint characterization results because of dividing the result by normalization factor.

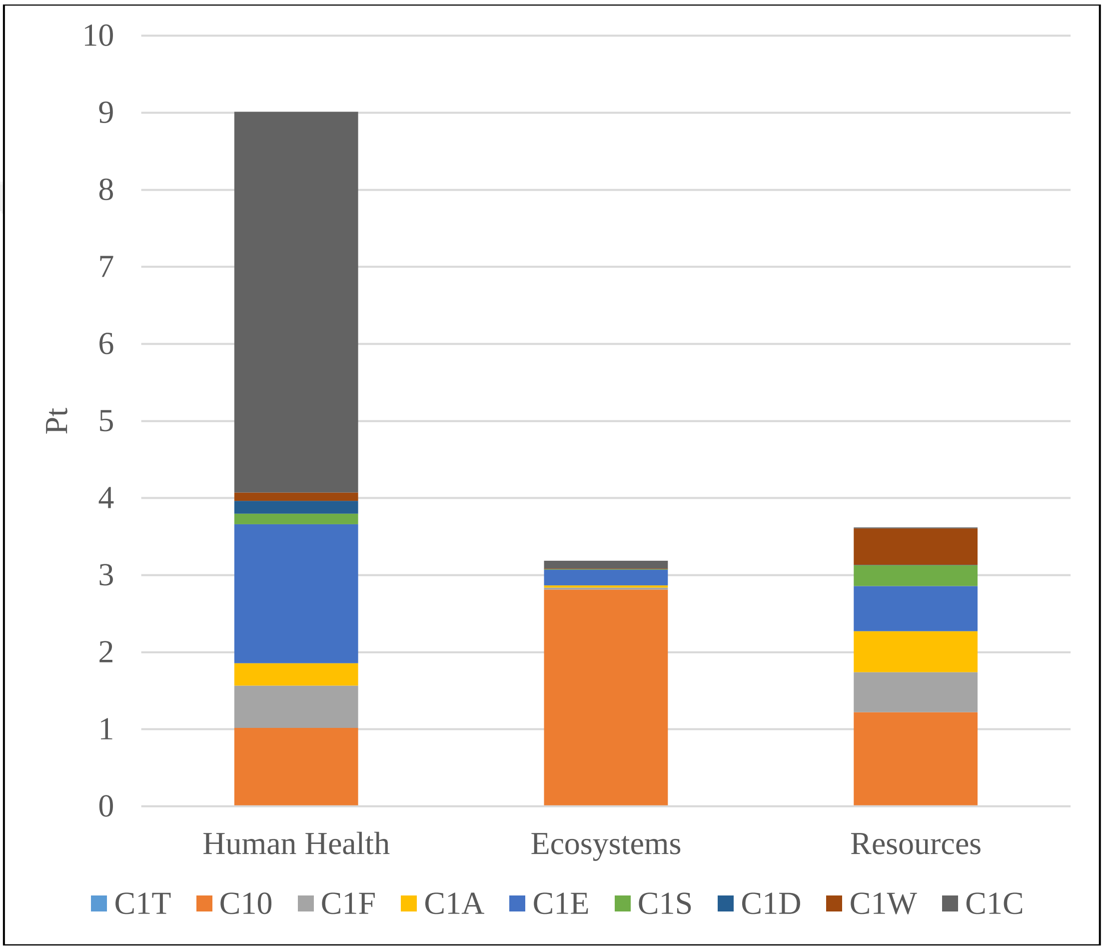


Figure 6.3 : Weighting of endpoint results of CS-1.

According to Figure 6.3 and Table 6.4, the highest impact of CS-1 on human health category (9.01286 Pt). At this category, cogeneration is the highest contributor with 4.940948 Pt. It is followed by enzyme production (1.807015716 Pt), organosolv pretreatment (1.0113013 Pt), furfural production (0.5514153 Pt), acetic acid recovery (0.287025 Pt), distillation (0.167787182 Pt), saccharification and fermentation (0.1357714 Pt), wastewater treatment (0.106420 Pt), and transportation (0.005181 Pt). Resources is 3.61808 Pt and formed by organosolv pretreatment (1.21220 Pt), enzyme production (0.583412 Pt), acetic acid recovery (0.532824 Pt), furfural production (0.5179512 Pt), wastewater treatment (0.471412 Pt), saccharification and fermentation (0.272003 Pt), cogeneration (0.01384 Pt), transportation (0.010105 Pt), and distillation (0.00433 Pt). Lastly, ecosystem category (3.187621 Pt) is formed by mainly organosolv pretreatment (2.81241 Pt), then enzyme production (0.206123 Pt), cogeneration (0.098789 Pt), acetic acid recovery (0.027805 Pt), furfural production (0.025382 Pt), wastewater treatment (0.01034 Pt), saccharification and fermentation (0.005502 Pt), transportation (0.000508 Pt) and distillation (0.000749 Pt).

Single score results presents the individual process total contributions and it is a new interpretation of weighting. It is illustrated in Figure 6.4.

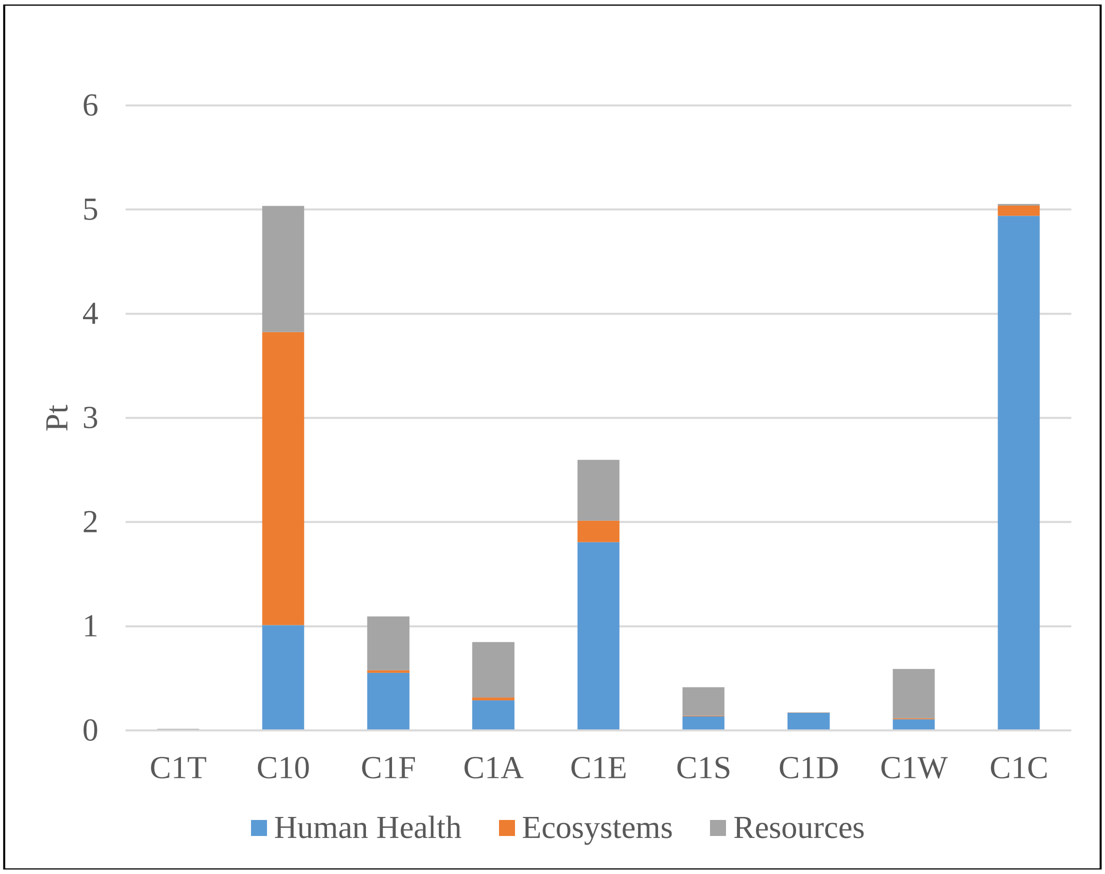


Figure 6.4 : Single score results of CS-1.

According to Figure 6.4, organosolv pretreatment has the highest impact for CS-1. Organosolv pretreatment mainly effects ecosystem, then human health and resources. The reason of the highest result is consuming more chemicals such as solvent and catalyst, requireing higher volumes than other processes, and forming solid wastes. Then cogeneration is the second contributor of CS-1. It mostly effects human health because of releasing combustion gases during the process. Next, enzyme production has higher contributions. Gases which produced by enzyme production, required different types and quantities of chemicals increased the impacts on human health, ecosystem and resource. Also, furfural production, acetic acid recovery and wastewater treatment, saccharification and fermentation, distillation and transportation have comparatively lower impacts on environment.

6.2 Analysis of CS-2

Analysis of CS-2 present as midpoint characterization results in Figure 6.5 and Table 6.5. Midpoint normalization results are given in Figure 6.6 and Table 6.6. Endpoint weighting results are shown in Figure 6.7 and Table 6.7 and lastly, single score results is given in Figure 6.8.

According to midpoint characterization results which is presented in Figure 6.5 and Table 6.5, organosolv pretreatment has the highest impact on CC (15.3554 kg CO_{2eq}.), OD (1.87E-06 kg CFC-11_{eq}.), HT (2.266893 kg 1,4-$DB_{eq.}$), IR (2.230304 kg U_{235eq}.), FE (0.002631 kg P_{eq}.), MEC (0.046466 kg 1,4-$DB_{eq.}$), ALO (483.7073 m^2a), ULO (4.818193 m^2a), NLT (0.040413 m^2), WD (5.143921 m^3), MD (0.196617 kg Fe_{eq}.), and FD (5.489432 kg oil_{eq}). Cogeneration has the highest impact on POF (1.658656 kg NMVOC), PMF (0.981676 kg $PM10_{eq}$.), and TA (4.165005 kg SO_{2eq}.) categories. Wastewater treatment has the most contribution on ME category (0.833402 kg N_{eq}.)and lastly, enzyme production has the greatest impacts on FEC (0.090804 kg 1,4-$DB_{eq.}$) and TEC (0.368523 kg 1,4-$DB_{eq.}$) categories. Similar to CS-1, saccharification and fermentation process has negative results on CC (-1.29786 kg CO_{2eq}.), HT (-0.14923 kg 1,4-$DB_{eq.}$), FE (-0.00028 kg P_{eq}.), TEC (-0.00023 kg 1,4-$DB_{eq.}$), FEC (-0.0038 kg 1,4-$DB_{eq.}$), MEC (-0.00637 kg 1,4-$DB_{eq.}$), ULO (-0.00089 m^2a), and NLT (-3.2E-05 m^2). Thus, midpoint characterization results indicated that saccharification and fermentation process has positive impact on environment at these categories.

According to midpoint normalization results which is presented in Figure 6.6 and Table 6.6, while TA is the highest impact in CS-1, ME has the highest impact in CS-2 (0.173592). Then, TA (0.169777), PMF (0.102004), ALO (0.09558), MEC (0.076166), TEC (0.057881), FE (0.049525), FEC (0.04252), HT (0.037458), FD (0.011229), CC (0.0062), ULO (0.006749), IR (0.00462), NLT (0.003482), MD (0.000549), OD (0.000142), WD (0) have contributions in order.

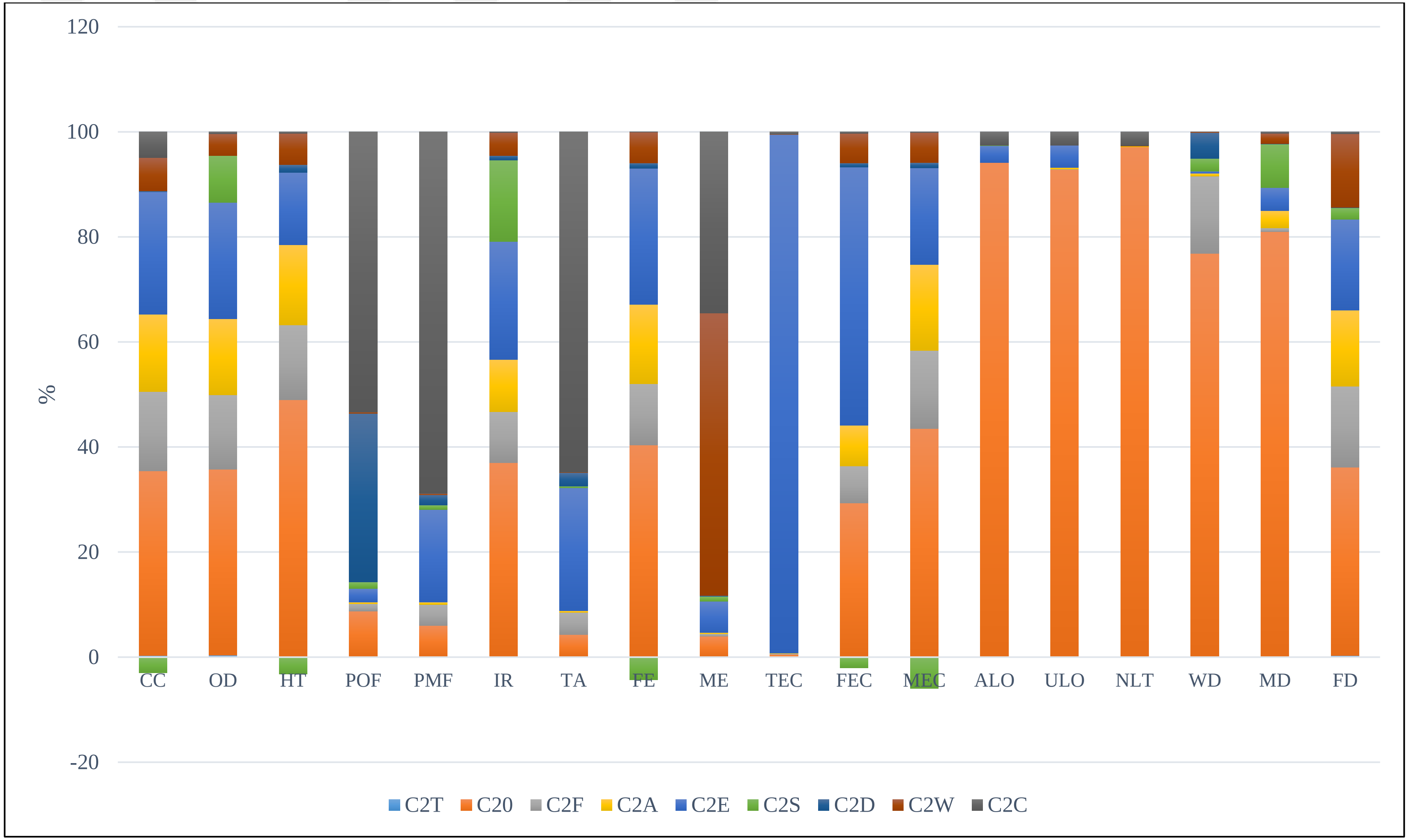


Figure 6.5 : Midpoint characterization results of CS-2.

Table 6.5 : Midpoint characterization results of CS-2.

Impact Category	Unit	Total	C2T	C20	C2F	C2A	C2E	C2S	C2D	C2W	C2C
CC	kg CO_{2eq}	42.46672	0.136514	15.3554	6.63596	6.447591	10.17947	-1.29786	0.069118	2.771288	2.169238
OD	kg CFC-11_{eq}	5.29E-06	2.05E-08	1.87E-06	7.5E-07	7.68E-07	1.17E-06	4.69E-07	3.42E-09	2.17E-07	2.08E-08
HT	kg 1,4-DB_{eq}	4.48599	0.002549	2.266893	0.659525	0.710187	0.636173	-0.14923	0.068875	0.277902	0.013119
POF	kg NMVOC	3.109559	0.00054	0.271942	0.042187	0.010712	0.080786	0.037688	0.998385	0.008662	1.658656
PMF	kg $PM10_{eq}$	1.424636	0.000148	0.085149	0.057679	0.005756	0.251321	0.01233	0.027976	0.002601	0.981676
IR	kg U_{235eq}	6.031352	0.001621	2.230304	0.586483	0.597126	1.357771	0.933157	0.05351	0.263707	0.007674
TA	kg SO_{2eq}	6.430962	0.000365	0.272926	0.273509	0.020174	1.50749	0.017839	0.165554	0.0081	4.165005
FE	kg P_{eq}	0.006245	1.68E-06	0.002631	0.000763	0.000987	0.001691	-0.00028	6.65E-05	0.000382	4.28E-06
ME	kg N_{eq}	1.549932	0.000177	0.061261	0.00748	0.003218	0.092167	0.014348	0.002854	0.833402	0.535023
TEC	kg 1,4-DB_{eq}	0.373423	1.83E-05	0.001904	0.000505	0.000543	0.368523	-0.00023	0.000135	0.000173	0.001855
FEC	kg 1,4-DB_{eq}	0.180938	8.9E-05	0.054121	0.012978	0.014327	0.090804	-0.0038	0.001512	0.01041	0.000496
MEC	kg 1,4-DB_{eq}	0.100748	0.000159	0.046466	0.015925	0.017471	0.019753	-0.00637	0.001038	0.006116	0.000189
ALO	m^2a	513.8688	6.72E-06	483.7073	0.001879	0.005567	16.65324	0.075673	0.005395	0.001334	13.41842
ULO	m^2a	5.191662	4.93E-06	4.818193	0.005201	0.017155	0.217419	-0.00089	0.000207	0.000881	0.133486
NLT	m^2	0.041595	2.52E-08	0.040413	2E-05	5.93E-05	1.03E-05	-3.2E-05	1.4E-06	3.22E-06	0.00112
WD	m^3	6.693794	0.000123	5.143921	0.986763	0.032147	0.029393	0.163769	0.325948	0.010379	0.00135
MD	kg Fe_{eq}	0.242782	5.84E-06	0.196617	0.001769	0.007847	0.01067	0.020204	0.000158	0.004734	0.000777
FD	kg oil_{eq}	15.31944	0.046002	5.489432	2.364605	2.218102	2.643621	0.338377	0.01969	2.14289	0.056726

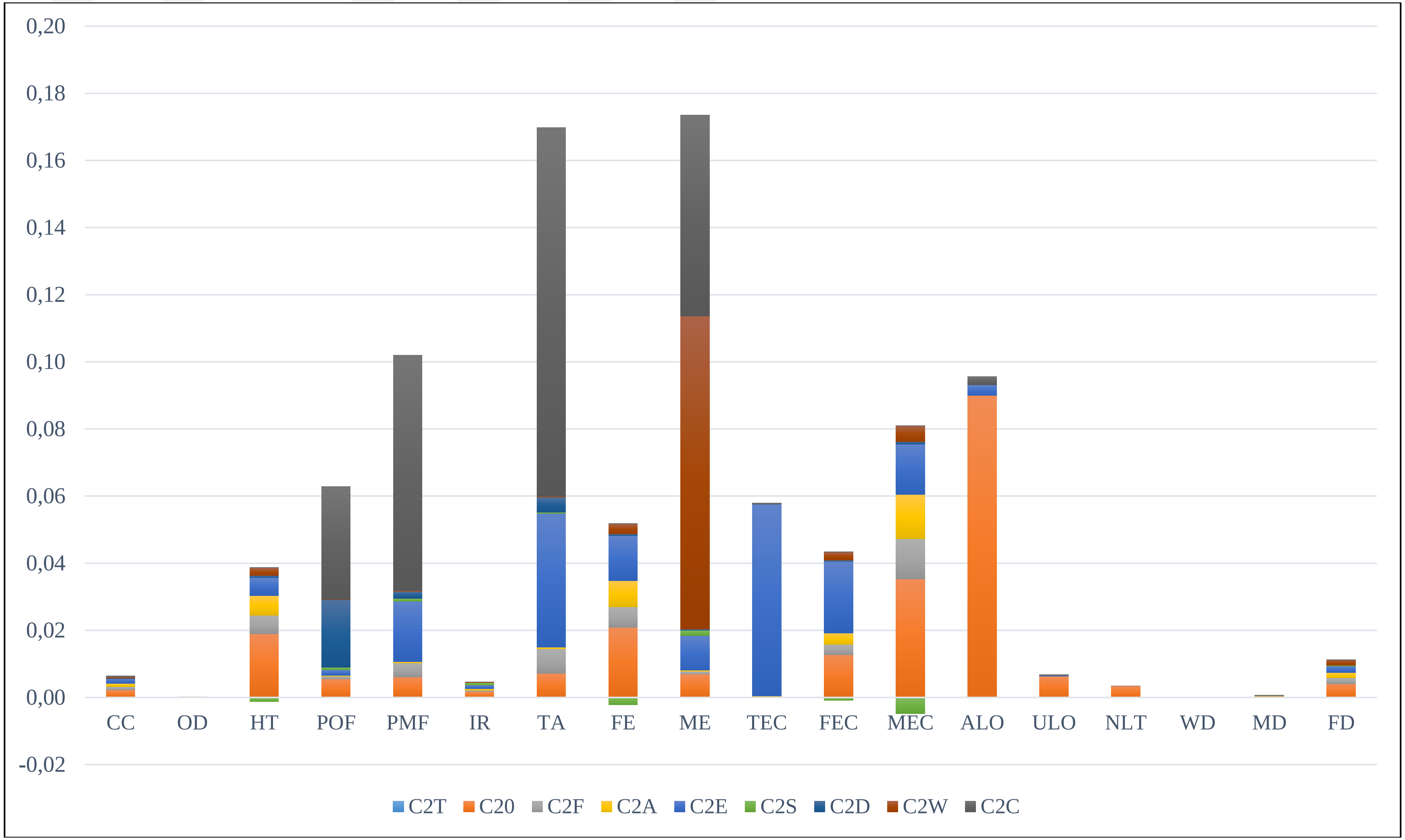


Figure 6.6 : Normalization of midpoint results of CS-2.

Table 6.6 : Normalization of midpoint results of CS-2.

Impact Category	Total	C2T	C20	C2F	C2A	C2E	C2S	C2D	C2W	C2C
CC	0.0062	1.99E-05	0.002242	0.000969	0.000941	0.001486	-0.00019	1.01E-05	0.000405	0.000317
OD	0.000142	5.5E-07	5.01E-05	2.01E-05	2.06E-05	3.14E-05	1.26E-05	9.16E-08	5.82E-06	5.58E-07
HT	0.037458	2.13E-05	0.018929	0.005507	0.00593	0.005312	-0.00125	0.000575	0.00232	0.00011
POF	0.062813	1.09E-05	0.005493	0.000852	0.000216	0.001632	0.000761	0.020167	0.000175	0.033505
PMF	0.102004	1.06E-05	0.006097	0.00413	0.000412	0.017995	0.000883	0.002003	0.000186	0.070288
IR	0.00462	1.24E-06	0.001708	0.000449	0.000457	0.00104	0.000715	4.1E-05	0.000202	5.88E-06
TA	0.169777	9.64E-06	0.007205	0.007221	0.000533	0.039798	0.000471	0.004371	0.000214	0.109956
FE	0.049525	1.33E-05	0.020864	0.006049	0.007829	0.013406	-0.00223	0.000527	0.00303	3.39E-05
ME	0.173592	1.99E-05	0.006861	0.000838	0.00036	0.010323	0.001607	0.00032	0.093341	0.059923
TEC	0.057881	2.83E-06	0.000295	7.83E-05	8.41E-05	0.057121	-3.6E-05	2.09E-05	2.68E-05	0.000287
FEC	0.04252	2.09E-05	0.012718	0.00305	0.003367	0.021339	-0.00089	0.000355	0.002446	0.000117
MEC	0.076166	0.00012	0.035128	0.01204	0.013208	0.014933	-0.00482	0.000785	0.004624	0.000143
ALO	0.09558	1.25E-09	0.08997	3.5E-07	1.04E-06	0.003098	1.41E-05	1E-06	2.48E-07	0.002496
ULO	0.006749	6.41E-09	0.006264	6.76E-06	2.23E-05	0.000283	-1.2E-06	2.69E-07	1.14E-06	0.000174
NLT	0.003482	2.11E-09	0.003383	1.67E-06	4.97E-06	8.64E-07	-2.7E-06	1.18E-07	2.7E-07	9.37E-05
WD	0	0	0	0	0	0	0	0	0	0
MD	0.000549	1.32E-08	0.000444	4E-06	1.77E-05	2.41E-05	4.57E-05	3.57E-07	1.07E-05	1.76E-06
FD	0.011229	3.37E-05	0.004024	0.001733	0.001626	0.001938	0.000248	1.44E-05	0.001571	4.16E-05

Table 6.7 : Weighting of endpoint results of CS-2.

Damage Category	Unit	Total	C2T	C20	C2F	C2A	C2E	C2S	C2D	C2W	C2C
Total	Pt	16.09297	0.015796	4.89116	1.100079	0.759781	2.580087	0.099582	0.172004	0.588257	5.886221
Human Health	Pt	9.695774	0.005181	1.01328	0.554165	0.246899	1.791889	0.0292	0.166926	0.106436	5.781798
Ecosystems	Pt	3.027198	0.000509	2.671622	0.025503	0.024468	0.206039	-0.00399	0.000747	0.010342	0.091962
Resources	Pt	3.369993	0.010106	1.206257	0.52041	0.488414	0.582159	0.074375	0.004331	0.471479	0.012462

For making clear comparison of endpoint categories, endpoint caharacterization results reduced by weighting factors. Endpoint weighting results are given in Figure 6.7 and Table 6.7.

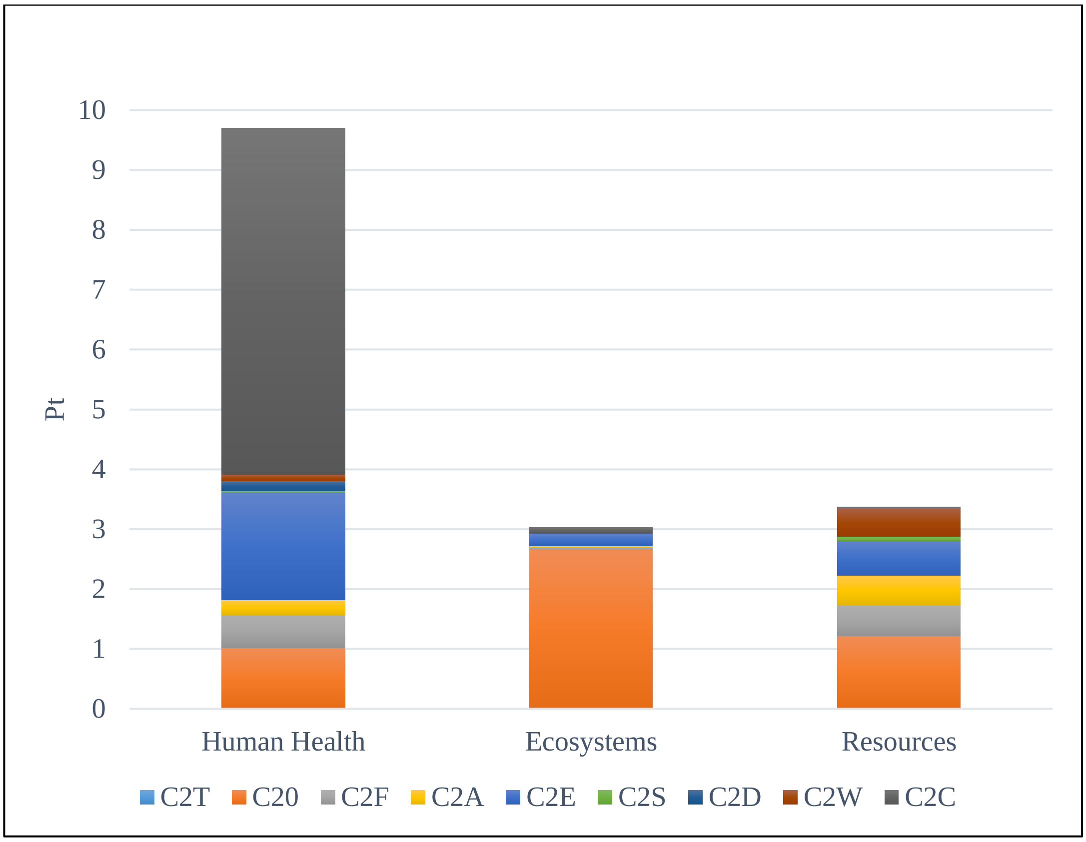


Figure 6.7 : Weighting of endpoint results of CS-2.

Weighting of endpoint results shows that, the highest impact of CS-2 on human health category, instead of ecosystem category in CS-1. While human health category is 9.695774 Pt, resource and ecosystem categories are 3.369993 Pt and 3.027198 Pt, respectively. The major contributor on human health is formed by cogeneration (5.781798 Pt). Then, enzyme production (1.791889 Pt), organosolv pretreatment (1.01328 Pt), furfural production (0.554165 Pt), and acetic acid recovery (0.246899 Pt), distillation (0.166926 Pt), wastewater treatment (0.106436 Pt), saccharification and fermentation (0.0292 Pt), and transportation (0.005181 Pt). Resource category results are formed by mainlu organosolv pretreatment (1.206257 Pt), then, enzyme production (0.582159 Pt), furfural production (0.52041 Pt), acetic acid recovery (0.488414 Pt), wastewater treatment (0.471479 Pt), saccharification and fermentation (0.074375 Pt), cogeneration (0.012462 Pt), transportation (0.010106 Pt), and distillation (0.004331 Pt). Lastly, at ecosystem category, 88.25% of contribution is formed by organosolv pretreatment (2.671622 Pt). Next, enzyme production has 6.8% of contribution (0.206039 Pt). Other processes contributions are lower than 0.1 Pt.

Endpoint caharacterization results are converted to single score results to compare each process impacts, individually. The results of single score and weighting results are same. The only difference in interpretation. Figure 6.8 presents the single score results of CS-2.

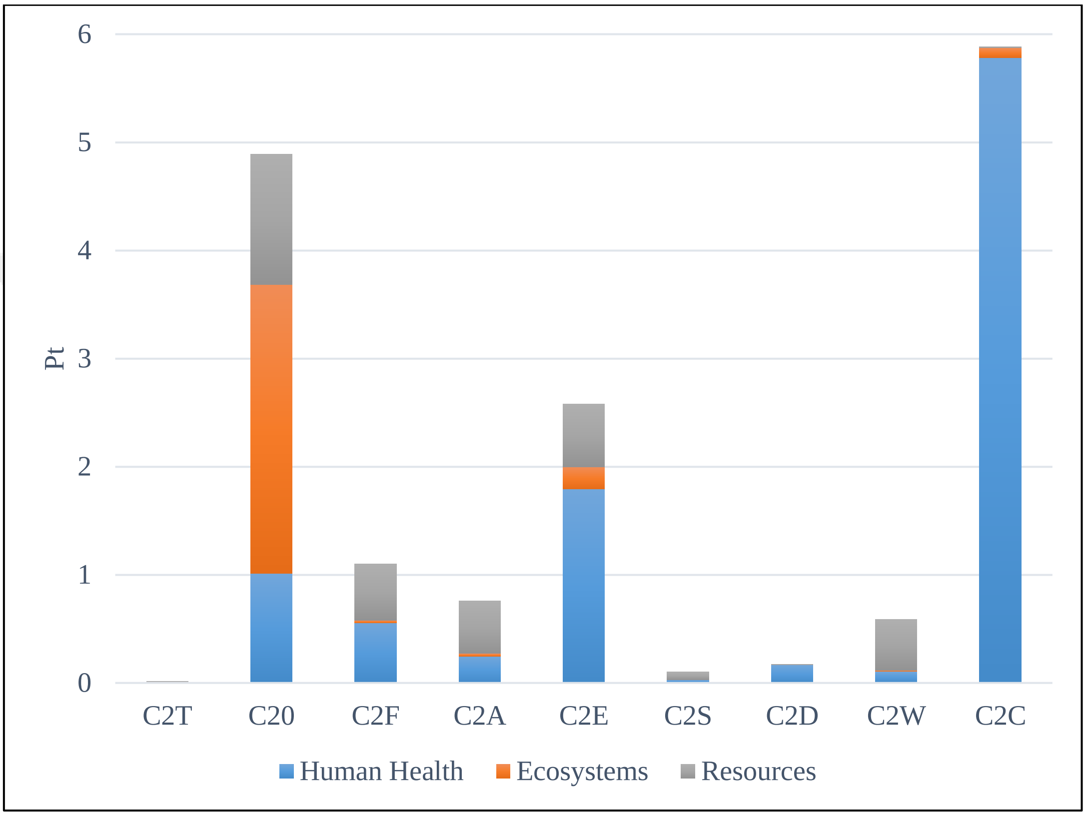


Figure 6.8 : Single score results of CS-2.

Single score results clarified the reason of the highest human health result is formed by cogeneration process. The contribution of cogeneration is higher than other processes. Organosolv pretreatment is the second place in order. Organosolv pretreatment impacts are both ecosystem, resources and human health category. Next, enzyme production has the highest contibution on human health, resources and slightly impact on resource category. The impacts of furfural production is both human health and resource category. On ecosystem category, impact of the furfural production is comparatively very small. Acetic acid recovery and wastewater treatment results are similar to acetic acid recovery process. The least contibutions are formed by transportation, saccharification and distilation processes.

6.3 Analysis of CS-3

CS-3 is a literature study which includes detailed Aspen Plus flowstreams of organosolv based biorefinery. It is a reminder that only Aspen Plus simulation software results are given in the original article and LCA study is done through this study similar to CS-1 and CS-2. CS-3 does not include enzyme production and waste water treatment processes. In addition, the all outputs are not defined in cogeneration process. Lastly, furfural part is different in CS-3 from CS-1 and CS-2. Furfural recovery process is designed in CS-3 instead of furfural production process in CS-1 and CS-2. However, the article which used as reference for CS-3 is the most similar, detailed, and reachable literature article. The feasible assumptions are done to complete missing data.

In this section, midpoint characterization results are shown in Figure 6.9 and Table 6.8. normalization of midpoint results are given in Figure 6.10 and Table 6.9. Weighting of endpoint results presented in Figure 6.11 and Table 6.10, and lastly, single score results are given in Figure 6.12.

According to midpoint characterization results, organosolv pretreatment has the highest contribution on all categories except POF and FEC. These categories are CC (20.22149 kg $CO_{2eq.}$), OD (4.99E-06 kg CFC-$11_{eq.}$), HT (1.785633 kg 1,4-$DB_{eq.}$), PMF (0.091667 kg $PM10_{eq.}$), IR (2.485227 kg $U_{235eq.}$), TA (0.266237 kg $SO_{2eq.}$), FE (0.001904 kg $P_{eq.}$), ME (0.076184 kg $N_{eq.}$), TEC (0.001672 kg 1,4-$DB_{eq.}$), MEC (0.039403 kg 1,4-$DB_{eq.}$), ALO (1004.006 m^2a), ULO (9.826756 m^2a), NLT (0.066173 m^2), WD (6.020022 m^3), MD (0.287158 kg $Fe_{eq.}$), and FD (13.33892 kg $oil_{eq.}$). The reason of these is cogeneration process has not fully developed data. 49.08% of POF result is formed by distillation process (0.629645 kg NMVOC). The, organosolv pretreatment and enzyme production have major impact on POF category with the results of 0.297884 kg NMVOC and 0.27376 kg NMVOC, respevtively. Other processes contribution are lower than 0.2 kg NMVOC. Wastewater treatment has the highest impact on FEC category (0.071286 kg 1,4-$DB_{eq.}$). Then organosolv pretreatment and cogeneration process follow wastewater treatment with the results of 0.047535 kg 1,4-$DB_{eq.}$ and 0.021637 kg 1,4-$DB_{eq.}$, respectively. There are any negative results are found in CS-3, therefore any processes in CS-3 have positive impacts on environment.

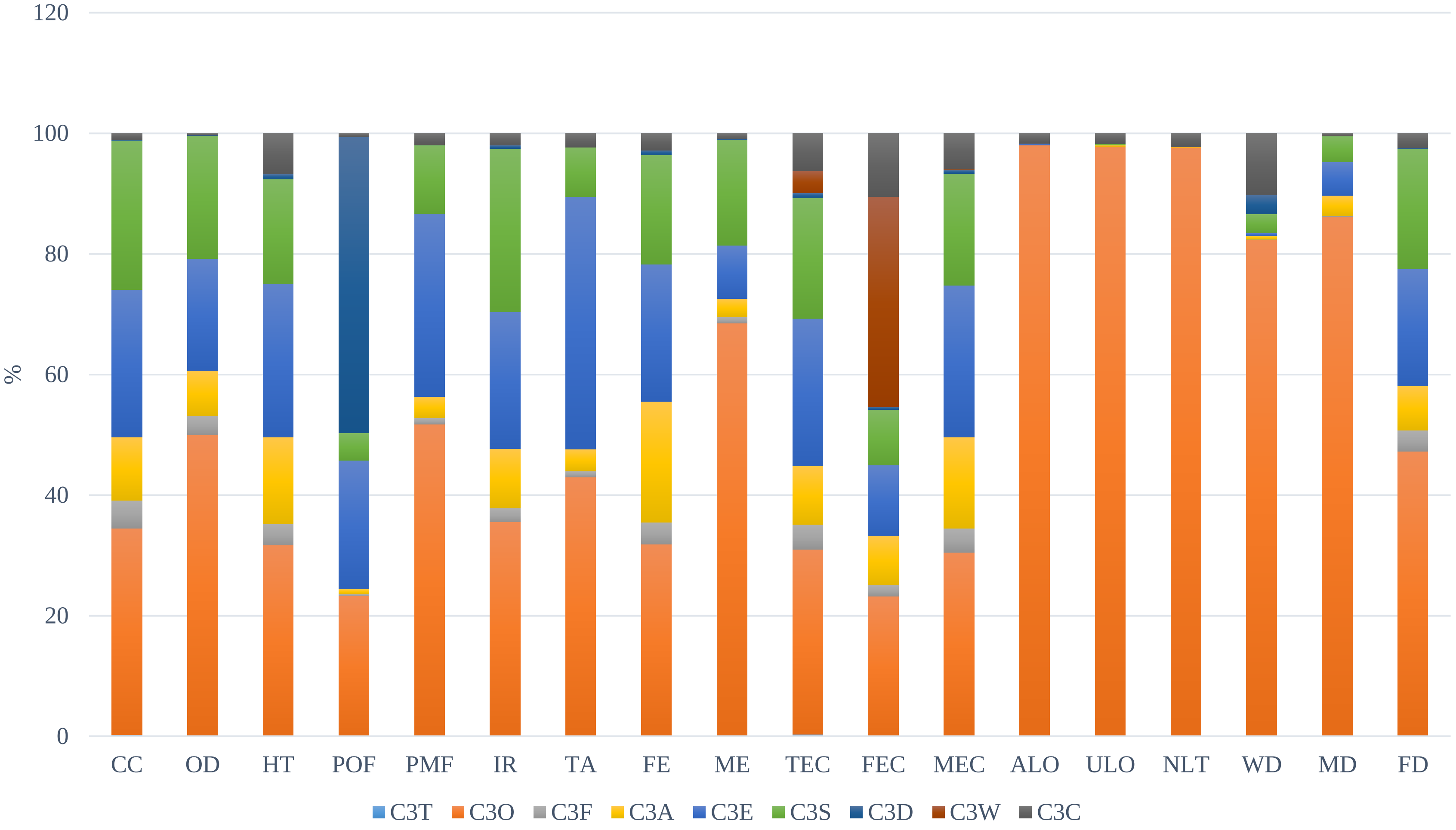


Figure 6.9 : Midpoint characterization results of CS-3.

Table 6.8 : Midpoint characterization results of CS-3.

Impact Category	Unit	Total	C3T	C3O	C3F	C3A	C3E	C3S	C3D	C3W	C3C
CC	kg CO_{2eq}	59.03655	0.136514	20.22149	2.754486	6.173256	14.43195	14.61394	0.048931	0	0.655979
OD	kg CFC-11_{eq}	1E-05	2.05E-08	4.99E-06	3.09E-07	7.59E-07	1.86E-06	2.05E-06	2.42E-09	0	3.54E-08
HT	kg 1,4-DB_{eq}	5.640439	0.002549	1.785633	0.198909	0.809633	1.431772	0.983181	0.047225	0	0.381538
POF	kg NMVOC	1.282825	0.00054	0.297884	0.004025	0.010941	0.27376	0.058544	0.629615	0	0.007517
PMF	kg $PM10_{eq}$	0.177375	0.000148	0.091667	0.001813	0.006312	0.053784	0.020197	6.48E-05	0	0.003389
IR	kg U_{235eq}	6.995957	0.001621	2.485227	0.160621	0.688958	1.585067	1.898216	0.037881	0	0.138367
TA	kg SO_{2eq}	0.620023	0.000365	0.266237	0.006171	0.022353	0.259428	0.050919	0.000207	0	0.014343
FE	kg P_{eq}	0.005982	1.68E-06	0.001904	0.000218	0.001198	0.001361	0.001084	4.71E-05	0	0.000168
ME	kg N_{eq}	0.111425	0.000177	0.076184	0.001144	0.003368	0.009872	0.019538	4.1E-05	0	0.001101
TEC	kg 1,4-DB_{eq}	0.005454	1.83E-05	0.001672	0.000226	0.000527	0.001334	0.001091	4.55E-05	0.000202	0.000338
FEC	kg 1,4-DB_{eq}	0.204937	8.9E-05	0.047535	0.00369	0.016734	0.024059	0.018846	0.001061	0.071286	0.021637
MEC	kg 1,4-DB_{eq}	0.129652	0.000159	0.039403	0.005186	0.019554	0.032655	0.024072	0.000732	0.000212	0.00768
ALO	m^2a	1024.009	6.72E-06	1004.006	0.000263	0.007955	2.573469	0.028161	0.003819	0	17.38872
ULO	m^2a	10.04684	4.93E-06	9.826756	0.002399	0.022543	0.005836	0.015688	0.000147	0	0.173468
NLT	m^2	0.067768	2.52E-08	0.066173	8.26E-06	7.8E-05	2.79E-05	2.53E-05	9.94E-07	0	0.001454
WD	m^3	7.308722	0.000123	6.020022	0.002124	0.045185	0.036555	0.227768	0.230749	0	0.746197
MD	kg Fe_{eq}	0.333117	5.84E-06	0.287158	0.000427	0.011143	0.018508	0.014369	0.000112	0	0.001393
FD	kg oil_{eq}	28.31861	0.046002	13.33892	0.991358	2.069424	5.497668	5.659042	0.013939	0	0.702265

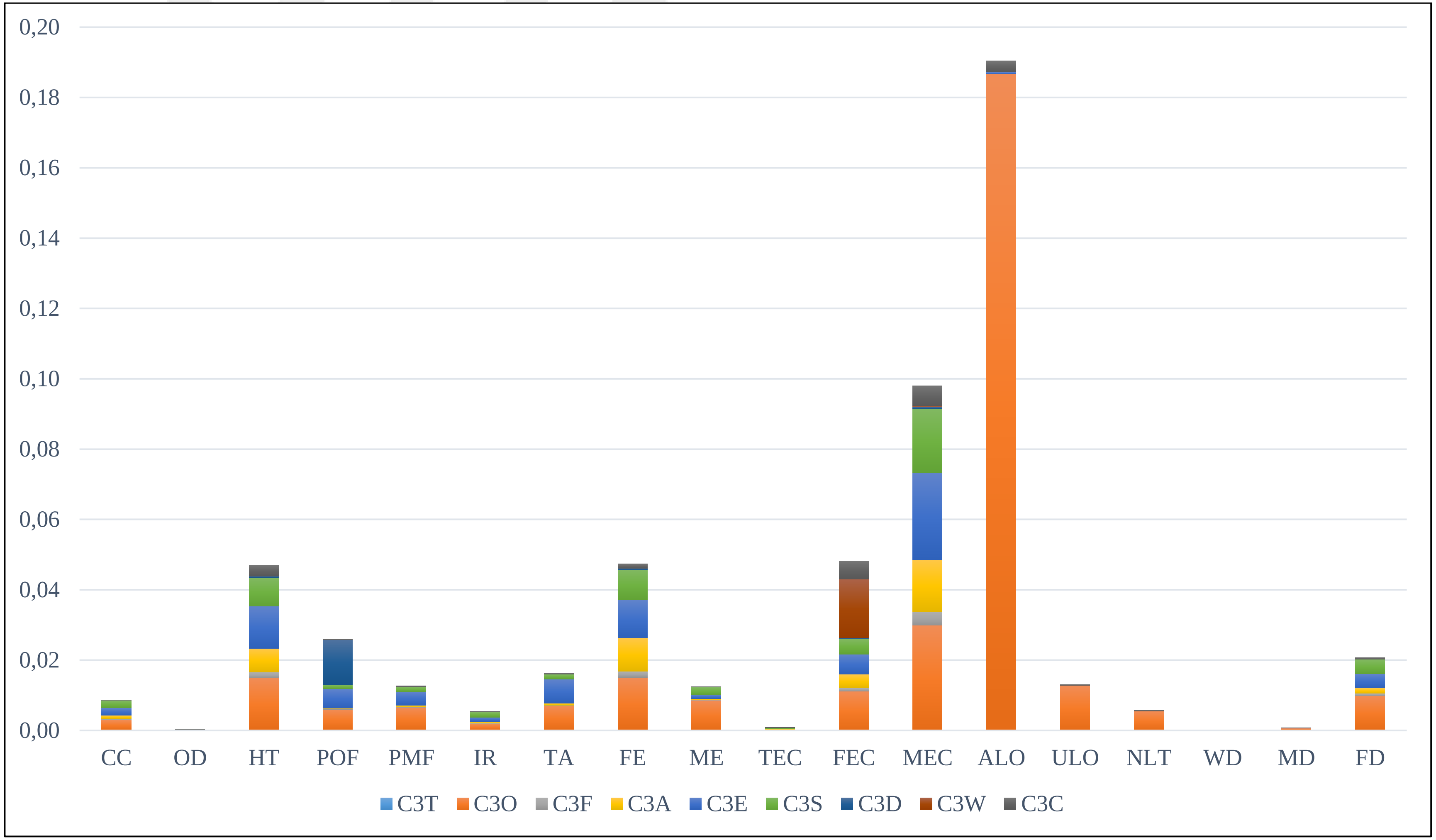


Figure 6.10 : Normalization of midpoint results of CS-3.

Table 6.9 : Normalization of midpoint results of CS-3.

Impact Category	Total	C3T	C3O	C3F	C3A	C3E	C3S	C3D	C3W	C3C
CC	0.008619	1.99E-05	0.002952	0.000402	0.000901	0.002107	0.002134	7.14E-06	0	9.58E-05
OD	0.000269	5.5E-07	0.000134	8.27E-06	2.03E-05	4.99E-05	5.49E-05	6.49E-08	0	9.49E-07
HT	0.047098	2.13E-05	0.01491	0.001661	0.00676	0.011955	0.00821	0.000394	0	0.003186
POF	0.025913	1.09E-05	0.006017	8.13E-05	0.000221	0.00553	0.001183	0.012718	0	0.000152
PMF	0.0127	1.06E-05	0.006563	0.00013	0.000452	0.003851	0.001446	4.64E-06	0	0.000243
IR	0.005359	1.24E-06	0.001904	0.000123	0.000528	0.001214	0.001454	2.9E-05	0	0.000106
TA	0.016369	9.64E-06	0.007029	0.000163	0.00059	0.006849	0.001344	5.46E-06	0	0.000379
FE	0.047434	1.33E-05	0.015097	0.001727	0.009503	0.010796	0.008592	0.000373	0	0.001331
ME	0.01248	1.99E-05	0.008533	0.000128	0.000377	0.001106	0.002188	4.59E-06	0	0.000123
TEC	0.000845	2.83E-06	0.000259	3.5E-05	8.17E-05	0.000207	0.000169	7.05E-06	3.13E-05	5.24E-05
FEC	0.04816	2.09E-05	0.011171	0.000867	0.003932	0.005654	0.004429	0.000249	0.016752	0.005085
MEC	0.098017	0.00012	0.029789	0.003921	0.014783	0.024687	0.018199	0.000553	0.00016	0.005806
ALO	0.190466	1.25E-09	0.186745	4.89E-08	1.48E-06	0.000479	5.24E-06	7.1E-07	0	0.003234
ULO	0.013061	6.41E-09	0.012775	3.12E-06	2.93E-05	7.59E-06	2.04E-05	1.91E-07	0	0.000226
NLT	0.005672	2.11E-09	0.005539	6.91E-07	6.53E-06	2.34E-06	2.12E-06	8.32E-08	0	0.000122
WD	0	0	0	0	0	0	0	0	0	0
MD	0.000753	1.32E-08	0.000649	9.65E-07	2.52E-05	4.18E-05	3.25E-05	2.53E-07	0	3.15E-06
FD	0.020758	3.37E-05	0.009777	0.000727	0.001517	0.00403	0.004148	1.02E-05	0	0.000515

Table 6.10 : Weighting of endpoint results of CS-3.

Damage Category	Unit	Total	C3T	C3O	C3F	C3A	C3E	C3S	C3D	C3W	C3C
Total	Pt	14.951339	0.015796	9.616238	0.328642	0.722422	2.071580	1.892623	0.006489	0.000021	0.297529
Human Health	Pt	2.974504	0.005181	1.196431	0.100050	0.243130	0.788476	0.591716	0.003215	0.000000	0.046306
Ecosystems	Pt	5.742036	0.000509	5.483371	0.010287	0.023632	0.072512	0.055033	0.000208	0.000021	0.096462
Resources	Pt	6.234799	0.010106	2.936436	0.218304	0.455660	1.210591	1.245874	0.003066	0.000000	0.154762

According to normalization midpoint characterization results that presented in Figure 6.10 and Table 6.9, the highest environmental impact category is ALO (0.190466) and it is formed by 98.04% of organosolv pretreatment and 1.07% of cogeneration. Other processes have not significant impacts on ALO category. The second highest category is MEC (0.098017) and contains organosolv pretreatment (0.029789), enzyme production (0.024687), saccharification and fermentation (0.018199), acetic acid recovery (0.014783), cogeneration (0.005806), and fermentation (0.003921). FEC (0.04816), HT (0.047098), and FE (0.047434) have similar normalization results. However, process contributions are different. The categories of OD, TEC, WD, and MD have minor impacts on environment.

Next step, damage assessment result is weighted by weighting factor to make more pointed comparison. Figure 6.11 and Table 6.10 present the weighting results of endpoint characterization results.

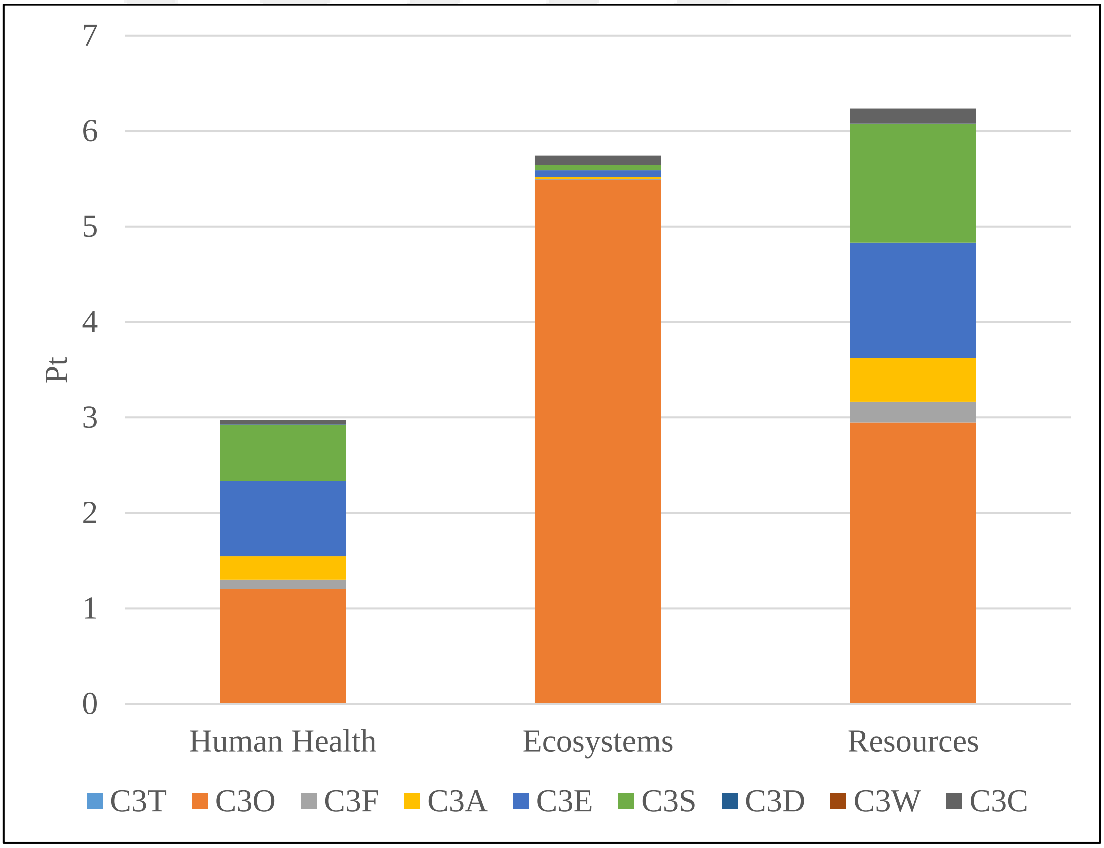


Figure 6.11 : Weighting of endpoint results of CS-3.

According to weighting of endpoint results, the highest impact is resources category (6.234799 Pt) and it is formed by 45% of organosolv pretreatment and the impact result is 2.936436 Pt. Organosolv pretreatment result is extremely higher than other processes results. The second contribution is formed by enzyme production and the result is 1.210591 Pt. In addition, ecosystems and human health have similar results such as 5.483371 Pt and 1.196431 Pt, respectively. At these two categories, organosolv pretreatment has the highest impact.

Lastly, weighting results are converted to understand individual process contribution on environment. Single score results are given in Figure 6.12.

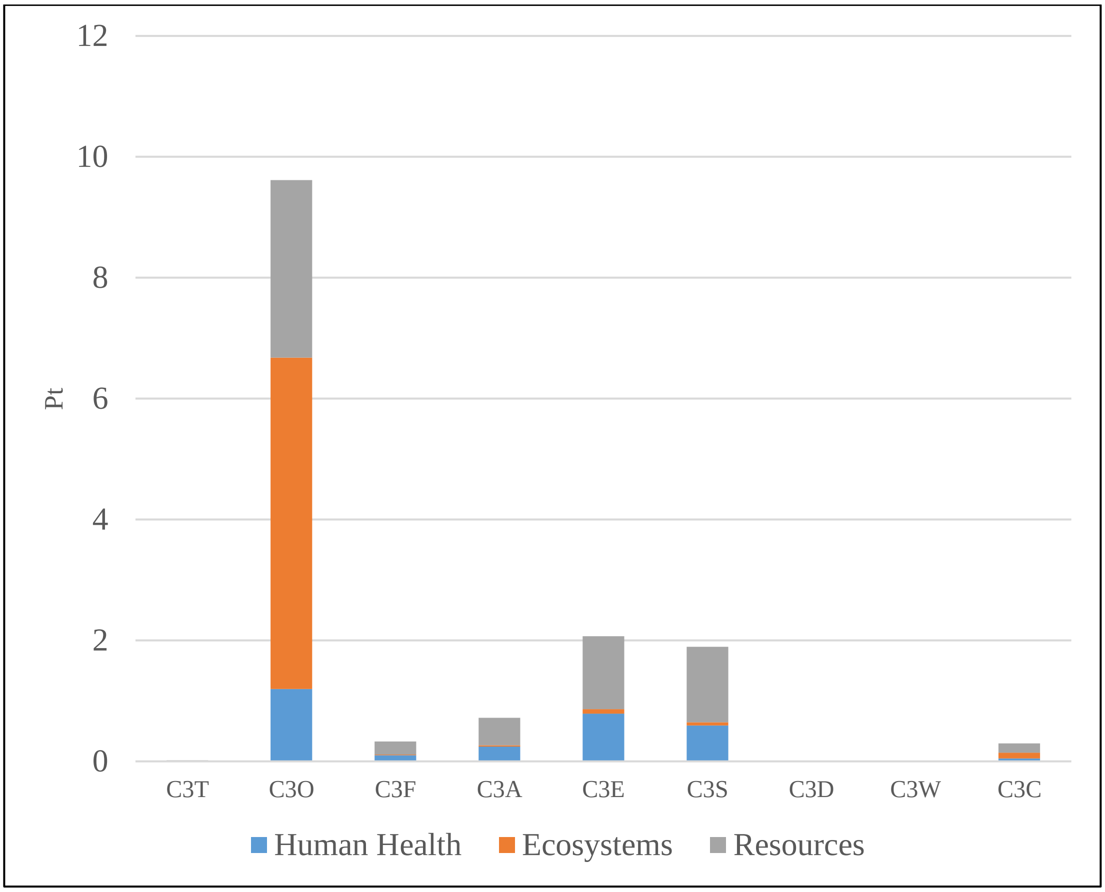


Figure 6.12 : Single score results of CS-3.

According to single score results of CS-3, the total impact of CS-3 on environment is 14.951339 Pt. Organosolv pretreatment (9.616238Pt) are the most significant contributor on environment. 64.31% of total impacts are formed by organosolv pretreatment. As it is stated weighting results, organosolv pretreatment effects ecosystem category, mainly. The second contribution which is mainly lower than organosolv pretreatment is formed by enzyme production (2.071580 Pt). Next, saccharification and fermentation process, acetic acid recovery and furfural production are follow them with the results of 1.892623 Pt, 0.722422 Pt, and 0.328642 Pt respectively. Other processes such as transportation, furfural production, distillation and wastewater treatment are lower than 0.25 Pt and have very slightly impact on environment.

6.4 Comparison of CS-1, CS-2, and CS-3

Analyzing CS-1, CS-2, and CS-3 give the results of environmental impacts of each process on impacts categories, while the comparison section presents the comparison of total impacts of CS-1, CS-2, and CS-3. This section provides to understand each case studies environmental impacts and makes a clear comparisons of CS-1, CS-, and CS-3.

Figure 6.13 and Table 6.11 presents the midpoint characterization comparison of CS-1, CS-2, and CS-3. According to midpoint characterization results, CS-3 has the highest impact on CC (59.03655 kg $CO_{2eq.}$), OD (1E-05 kg CFC-$11_{eq.}$), HT (5.640439 kg 1,4-$DB_{eq.}$), IR (6.995957 kg $U_{235eq.}$), FEC (0.204937 kg 1,4-$DB_{eq.}$), MEC (0.129652 kg 1,4-$DB_{eq.}$), ALO (1024.009 m^2a), ULO (10.04684 m^2a), NLT (0.067768 m^2), WD (7.308722 m^3), MD (0.333117 kg $Fe_{eq.}$), and FD (28.31861 kg $oil_{eq.}$) categories. The highest impact on POF (3.109559 kg NMVOC), PMF (1.424636 kg $PM10_{eq.}$), TA (6.430962 kg $SO_{2eq.}$), FE (0.006245 kg $P_{eq.}$), ME (1.549932 kg $N_{eq.}$), and TEC (0.373423 kg 1,4-$DB_{eq.}$) categories is formed by CS-2. CS-1 has the highest impact on any categories. Generally, CS-1 results are slightly lower than CS-2 results. While 85% or more similarity exists at IR, FE, and WD categories, 85% or more difference are found at PMF, TA, ME, and TEC categories. The main differences are occurred by chemical production usage, design differences, and lackness of data of CS-3.

Nextly, normalization of midpoint caharacterization gives the comparable results of CS-1, CS-2, and CS-3 which presented in Figure 6.14. The most impacted category is ALO with the result of 0.19047 by CS-3. The next impacted categories are ME, TA, and PMF with the results of 0.17359, 0.16978, and 0.10200, respectively. Both these three categories, CS-2 is the highest contributor. In both 3 cases, CC (0.00862), OD (0.00027), IR (0.00536), ULO (0.00712), NLT (0.00567), WD (0), MD (0.00075), and FD (0.02076) have comparatively slightly impacts on environment. At these categories, the impact of CS-3 has more impacts than CS-1 and CS-2.

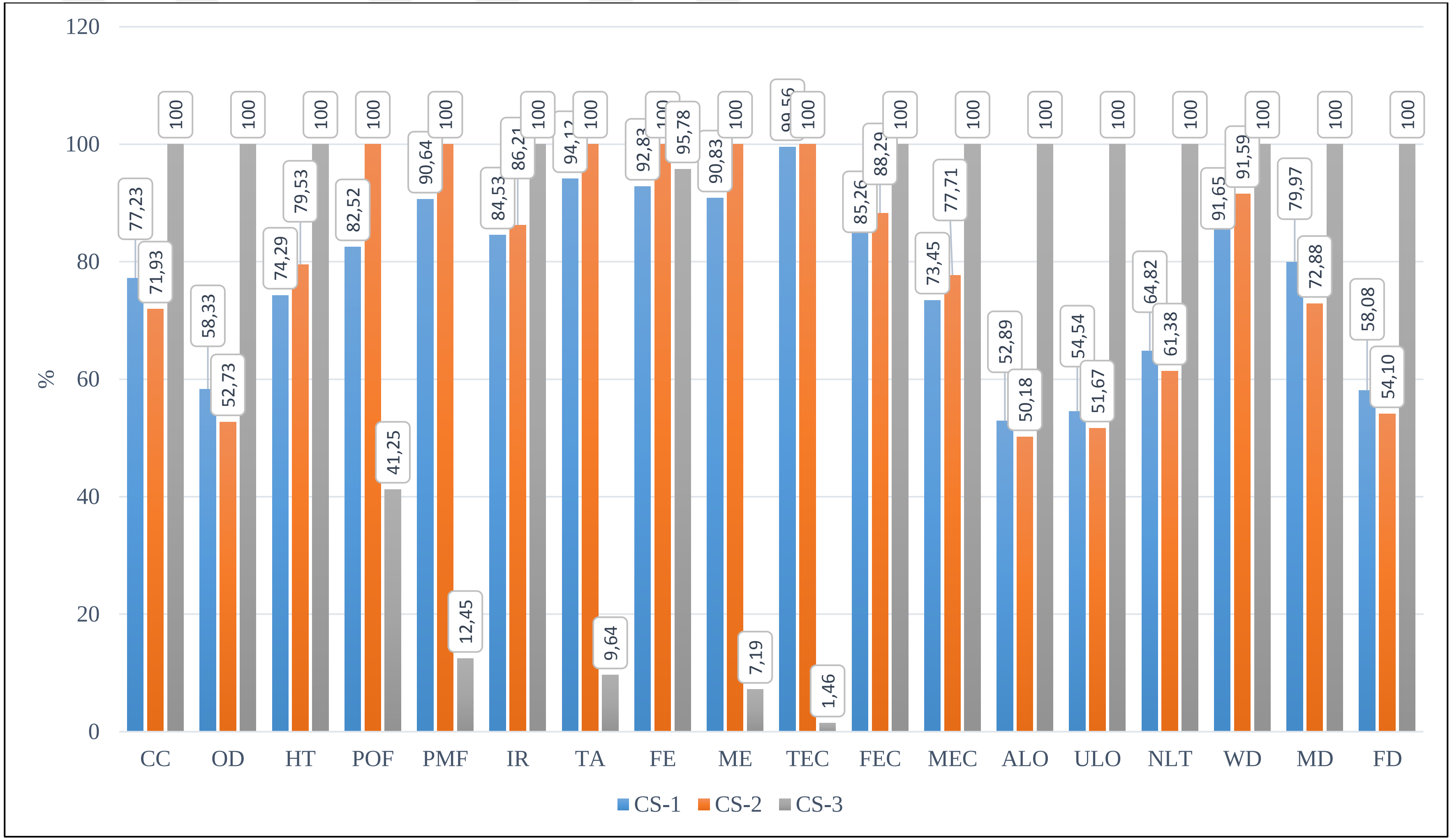


Figure 6.13 : Comparison of midpoint characterization results of CS-1, CS-2 and CS-3.

Table 6.11 : Comparison of midpoint characterization results of CS-1, CS-2, CS-3.

Impact Category	Unit	CS-1	CS-2	CS-3
CC	kg CO_{2eq}	45.5943	42.46672	59.03655
OD	kg CFC-11_{eq}	5.85E-06	5.29E-06	1E-05
HT	kg 1,4-DB_{eq}	4.190301	4.48599	5.640439
POF	kg NMVOC	2.565918	3.109559	1.282825
PMF	kg $PM10_{eq}$	1.291309	1.424636	0.177375
IR	kg U_{235eq}	5.913878	6.031352	6.995957
TA	kg SO_{2eq}	6.052871	6.430962	0.620023
FE	kg P_{eq}	0.005797	0.006245	0.005982
ME	kg N_{eq}	1.407827	1.549932	0.111425
TEC	kg 1,4-DB_{eq}	0.371787	0.373423	0.005454
FEC	kg 1,4-DB_{eq}	0.174731	0.180938	0.204937
MEC	kg 1,4-DB_{eq}	0.095235	0.100748	0.129652
ALO	m^2a	541.5526	513.8688	1024.009
ULO	m^2a	5.479088	5.191662	10.04684
NLT	m^2	0.043927	0.041595	0.067768
WD	m^3	6.698682	6.693794	7.308722
MD	kg Fe_{eq}	0.266393	0.242782	0.333117
FD	kg oil_{eq}	16.44724	15.31944	28.31861

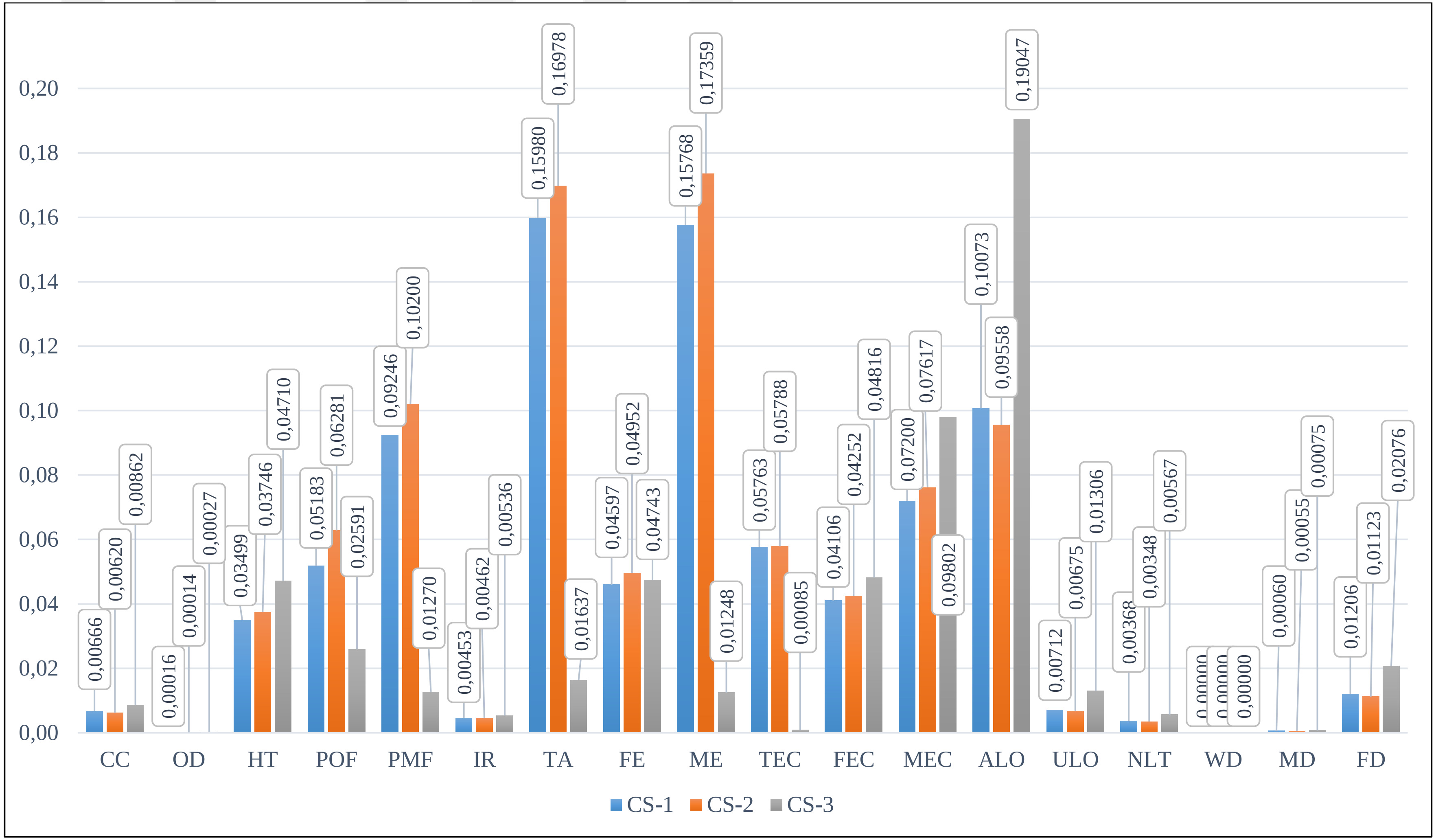


Figure 6.14 : Comparison of midpoint normalization results of CS-1, CS-2 and CS-3.

The weighting of endpoint results are given in Figure 6.15. These results indicate that CS-3 has the highest impact on ecosystem (5.74 Pt) and resource categories (6.23 Pt). At these categories, CS-1 (3.19 Pt and 3.62 Pt) and CS-2 (3.03 Pt and 3.37 Pt) follow CS-3, respectively. In contrast, CS-2 and CS-1 have similar and higher impact on human health category with the result of 9.7 Pt and 9.01 Pt. The weighting result of CS-3 on human health (2.97 Pt) category is comparatively smaller than CS-1 and CS-2.

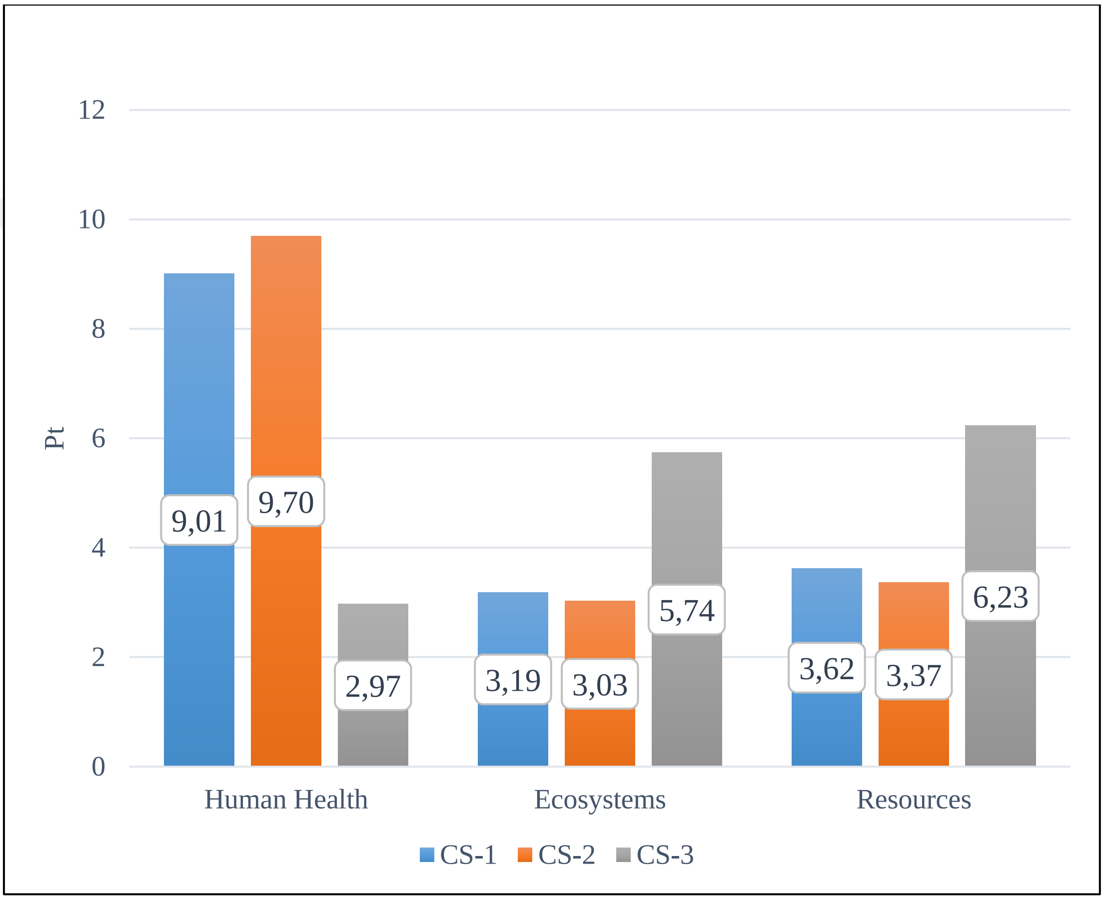


Figure 6.15 : Comparison of endpoint weighting results of CS-1, CS-2 and CS-3.

6.5 Interpretation

Interpretation is the last step of a LCA study. In this section, all cases and results are interpretating. According to interpretation, high impacted categories and the reasons are defined and new arrangement and calculations can be done to decrease the environmental impacts. The interpretation of this LCA study is determined and explained below.

1. According to CS-1 results, organosolv pretreatment is the highest contributor. For midpoint characterization indicators, CC, OD, HT, IR, MEC, ALO, ULO, NLT, WD, MD, and FD categories. Therefore, organosolv pretreatment is the highest contributor at ecosystem and resource categories. Cogeneration is the second contributor and the highest contributions on PMF and TA categories. Therefore, it increases the impact on human health. Enzyme production is in the third place and mostly effect to TEC, FEC, and FE categories. Except all categories, saccharification and fermentation process has positive impacts on HT, FE, TEC, FEC, NLT, and MEC categories.
2. CS-2 results present that organosolv pretreatment is the highest contributor on environment. For midpoint characterization indicators, CC, OD, HT, IR, MEC, FE, ALO, ULO, NLT, WD, MD, and FD categories. Therefore, organosolv pretreatment is the highest impact at ecosystem and resource categories. Cogeneration is the second contributor and the highest contributions on POF, PMF and TA categories. Therefore, it increases the impact on human health. Enzyme production is in the third place and mostly effect to TEC and FEC categories. Except all categories, saccharification and fermentation process has positive impacts on CC, HT, FE, TEC, FEC, NLT, ULO, and MEC categories.
3. The results of CS-3 show that organosolv pretreatment is the highest contributor on environment. For midpoint characterization indicators, CC, OD, HT, PMF, IR, TA, FE, ME, TEC, MEC, ALO, ULO, NLT, WD, MD, and FD categories. Therefore, organosolv pretreatment is the highest impact on both human health, ecosystem, and resource categories. Enzyme production is in the second place but comparatively very lower impact than organosolv pretreatment. In CS-3, there is any process have positive impact on environment.
4. According to analysis results, in both three cases organosolv pretreatment has the highest impact. Therefore, modifications such as solvent and catalyst usage reduction or alteration, process design modifications can be done to reduce environmental impacts. Also, cogeneration process have more impact than other process due to contain combustion. Combustion releases exhaust gases and particulate matter and these reasons increase the environmental impacts.
5. While comparing the total impact results, CS-1 is 15.82 Pt, CS-2 is 16.1 Pt, and CS-3 is 14.96 Pt. CS-3 has the highest impact on CC, OD, HT, IR, FEC,

MEC, ALO, ULO, NLT, WD, MD, and FD categories. The highest impact on POF, PMF, TA, FE, ME, and TEC categories is formed by CS-2. In addition, CS-2 has the highest impact on human health category and CS-3 has the highest impact on ecosystem and resource categories.

6. The results show the minimum impacts are formed by CS-3, CS-1 and CS-2, respectively. However, data lackness in CS-3 makes this comparasion untrustable. However, CS-1 has lower impact at data completed process such as organosolv pretreatment, furfural recovery, acetic acid recovery, saccharification and fermentation and distillation than CS-3.

According to LCA results, an overview is done over the IOBB, and organosolv pretreatment and cogeneration processes are found as huge contributors. The modification that reduces environmental impacts are determined.

In the organosolv pretreatment process:

- Catalyst usage can reduce the water consumption in lignin precipitation reactor.
- Reduction of reaction temperature and pressure cause low energy consumption.
- Energy efficient dryer usage in lignin drying section causes low energy consumption.

In the cogeneration process:

- Reduction of the water content of combusted feedstock causes efficient combustion and releases lower emissions.
- Selection of energy efficient oven causes efficient combustion.
- Longer heat exchanger selection provides the transfer of the heat between the reactor and air. Air is fed into the reactor in the appropriate temperature. Thus, the heat loss is prevented, and low energy consumption requires.

These modifications make the process cleaner and greener. The implication of modification contributes to the low carbon economy and makes the IOBB greenest. Although modifications reduce the environmental impacts, the main contributions occur from wood usage in organosolv pretreatment process and combustion gas releases in the cogeneration process. These inputs and outputs have higher impacts than other processes.

7. CONCLUSIONS AND RECOMMENDATIONS

In this thesis research, integrated organosolv based biorefinery (IOBB) that used SOC and IWS is designed to produce multi products. Then, LCA studies of simulated IOBB presented. Aspen Plus simulation software and SimaPro LCA software have been used in the study. This thesis research is the first study in Turkey and one of the limited study in the world to contain both Aspen Plus simulation and LCA study for biorefinery approach. Additionally, there is any existed third generation biorefinery, and this study will be the first in Turkey. This study proved that IOBB could apply industrial scale, and provides on-site energy production, improves energy security, contributes to the development of the chemical industry. In the end, it will be a guiding light to all concerned about biorefineries.

The conclusions achieved in the study are described below.

1. According to Aspen Plus simulation software results, when 5000 kg of feedstock is used in the IOBB, the products are produced as 1160 kg/h of bioethanol, 908 kg/h of organosolv lignin, 340 kg/h of furfural, 122 kg/h of acetic acid, 7495 kW of bioheat and 2139 kW of biopower for CS-1 and 1155 kg/h of bioethanol, 894 kg/h of organosolv lignin, 358 kg/h of furfural, 135 kg/h of acetic acid, 7223 kW of bioheat and 2064 kW of biopower for CS-2, respectively. The product ratio depends on the feedstock contents. High cellulose ratio increases bioethanol production; high hemicellulose ratio increases furfural production, high acetate ratio increase acetic acid production, and high lignin ratio increase lignin production. Also, solid, liquid and gas emissions are in Turkey’s permitted emissions limit range.

2. According to LCA results of each process for CS-1, CS-2, and CS-3, the highest impacts for CS-1 and CS-3 which is found in the literature is occurred from organosolv pretreatment and for CS-2 are occurred from the cogeneration process. The reason for this is that organosolv pretreatment includes grinding and chipping operations, a large amount of input (wood) used as feedstock.

Cogeneration emissions are not well defined in CS-3. Therefore cogeneration impacts are low in CS-3. Increasing chemical demand is improved the environmental impacts of processes. High chemical required processes such as organosolv process, enzyme production, furfural production have the highest impact on the environment.

3. The comparison of damage assessment results of CS-1, CS-2, and CS-3, the total environmental impacts are found as 15.82 Pt for CS-1, 16.1 Pt for CS-2, and 14.96 Pt for CS-3. While CS-2 has the highest impact on human health, CS-3 has the highest impact on the ecosystem and resources categories.

Summaries of recommendation on the thesis are explained below:

1. ISO standardizes LCA studies, and general rules are defined. However, these standards specify the guidelines and LCA practitioners are free to apply selections. Therefore, the results of each study based on the specific system selections such as system boundary, functional unit, and assumptions. It is remembered that the LCA results of this study are presented based on the selections that detailed and clearly described.
2. The selection of feedstock should be made regarding increase the most desired product. Therefore, the contents of the feedstock should be well defined. Besides, large amounts of feedstock decrease operational cost. The feedstock selection is made regarding supply chain. Feedstock is flexible in IOBB.
3. In Turkey, the usage of energy forestry is not widely developed. Therefore, this is an essential challenge for feedstock chain. Oak coppice forest is acceptable for energy forestry to spread the most second widely area. The government, research centers, and universities should be corporate to made usage of energy forestry widely. Also, mechanical treatment options should be increased to decrease energy consumption and environmental impacts.
4. In industry, IWS contains some additives such as glue. However, for biochemical conversion, it should be additive-free. Therefore, the selection of IWS is made regarding non-additive.
5. Aspen Plus simulation software contains cost calculation. However, it is difficult to trustable apply to Turkey’s condition. Especially for practitioners, cost calculations are important to the evaluation of profitability. In future work, detailed cost assessment can be done in future work.

6. The environmental impacts of integrated organosolv based biorefineries are taken from the Ecoinvent database. However, the database does not include up-to-date data from Turkey. Therefore, data are selected regarding the most acceptable methods inexperienced countries found in the literature. Thus, future work can be to prepare and apply LCI data based on Turkish data.
7. Fermentation and wastewater treatment include digestion reactors. The critical amount of CO_2 is released during these processes. Additional carbon captured processes are attached in the IOBB to decrease GWP in future work. Also, other value-added chemical processes such as 5-HMF recovery, from organosolv lignin to value-added chemical process could be added into the IOBB to decrease pollutants in wastewater.
8. In the eco-design approach, the significant contributions on the environment are determined and in the future detailed research of each process will be studied to obtained cleanest and greenest IOBB.
9. This study contributes to the literature to provide efficiency of the process, emission rates, and impacts on the environment. This study presents both simulation and LCA result as precise, detailed and transparent as possible.
10. The alternative application area of SOCs is presented in the study. According to this study results, authorities could decide to the dissemination of SOC forest to use as energy forestry. Therefore, SOC forest could be used to produce value-added materials instead of conventional heating.
11. Traditionally, IWS is used to produce chipboard in industry. However, this study provides an alternative usage area for IWS. Therefore, it provides an opportunity for the industrial practitioner to make a selection to IWS application.

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APPENDICES

APPENDIX A: Aspen Plus simulation software mass flows for CS-1 and CS-2.

APPENDIX B: Aspen Plus simulation software stream temperature and pressure for CS-1 and CS-2.

APPENDIX A

Following are the tables providing mass flows result that found in Aspen Plus simulation software. The studies about Aspen Plus simulation software are described in Chapter 3, in detail. While the tables from Table A.1 to Table A.17 present the results of CS-1, the tables from Table A.18 to Table A.35 show the results of CS-2.

To provide more readable tables, some components are merged under groups. These groups and their contents are:

- Other sugar monomers: Arabinose, Mannose, Galactose
- Sugar oligomers: Xylooligomers, Glucooligomers, Mannooligomers, Galactooligomers
- NO_x: NO, NO_2
- Other inorganic acids: Levulinic acid, Formic acid, Lactic acid, Succinic acid
- Other sugar polymers: Arabinan, Mannan, Galactan
- Nutrients: CNUTR and WNUTR
- Others: Extractives, carbon, oil
- Ash: Soluble and insoluble ash

Table A.1 : Aspen Plus simulation software mass flows for CS-1 (S1-S13).

Components	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13
Total flow	46.3	5000	63.75	30222.15	30222.15	30222.15	30222.15	27552.99	2669.157	27552.99	27552.99	65.164	27487.83
Glucose	0	0	0	0	0	0	10.108	10.108	0	10.108	30.324	0	30.324
Xylose	0	0	0	0	0	0	193.124	193.124	0	193.124	461.506	0	461.506
Soluble lignin	0	0	0	0	0	0	908.35	908.35	0	908.35	908.35	0	908.35
HMF	0	0	0	0	0	0	9.361	9.361	0	9.361	6.085	0	6.085
Oth. sugar mono.	0	0	0	0	0	0	236.144	236.144	0	236.144	332.915	0	332.915
Sugar olig.	0	0	0	0	0	0	413.457	413.457	0	413.457	0	0	0
Ethanol	6.2	0	0	12500	12500	12500	12500	12500	0	12500	12500	0	12500
Water	40.1	42.6	0	12701	12701	12701	12689.53	12689.53	0	12689.53	12644.22	0	12644.22
Furfural	0	0	0	0	0	0	119.107	119.107	0	119.107	119.107	0	119.107
H_2SO_4	0	0	63.75	63.75	63.75	63.75	63.75	63.75	0	63.75	63.75	0	63.75
N_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	0	0	0	0	0	0	57.594	57.594	0	57.594	129.587	0	129.587
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0	0	0	0	0	0	31.46	31.46	0	31.46	31.46	0	31.46
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	2006	0	2006	2006	2006	1946.612	0	1946.612	0	0	0	0
Xylan	0	772.5	0	772.5	772.5	772.5	149.378	0	149.378	0	0	0	0
Lignin	0	1227.5	0	1227.5	1227.5	1227.5	319.15	0	319.15	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	158.4	0	158.4	158.4	158.4	28.813	0	28.813	0	0	0	0
Oth. sugar poly.	0	509	0	509	509	509	201.727	0	201.727	0	0	0	0
Others	0	260.5	0	260.5	260.5	260.5	320.983	320.983	0	320.983	325.664	65.164	260.5
Ash	0	23.5	0	23.5	23.5	23.5	23.501	0.024	23.477	0.024	0.024	0	0.024

Table A.2 : Aspen Plus simulation software mass flows for CS-1 (S14-S26).

Components	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26
Total flow	13357.1	12693.3	3332.962	14130.73	399.987	399.987	3096.222	636.727	17326.62	31457.34	32094.07	31154.54
Glucose	0	0	0	30.324	0	0	0	0	0	30.324	30.324	30.294
Xylose	0	0	0	461.506	0	0	0	0	0	461.506	461.506	461.044
Soluble lignin	0	0	0	908.35	0	0	0	0	0	0	0	0
HMF	0.002	0.002	0	6.083	0	0	0	0	0	6.083	6.083	6.077
Oth. sugar mono.	0	0	0	332.915	0	0	0	0	0	332.915	332.915	332.583
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0	0
Ethanol	9256.68	8796.653	460.027	3243.32	0	0	46.328	413.699	0	3243.32	3657.019	3653.362
Water	4024.279	3824.285	199.994	8619.944	399.987	399.987	380.356	219.625	17326.62	25946.56	26166.18	26140.02
Furfural	52.533	49.922	2.611	66.574	0	0	0.263	2.348	0	66.574	68.922	68.853
H_2SO_4	0.001	0.001	0	63.749	0	0	0	0	0	63.749	63.749	63.686
N_2	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	21.136	20.085	1.05	108.451	0	0	0.106	0.945	0	108.451	109.396	109.286
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	2.47	2.348	0.122	28.99	0	0	0.012	0.11	0	28.99	29.1	29.071
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	1946.612	0	0	0	1946.612	0	0	0	0	0
Xylan	0	0	149.378	0	0	0	149.378	0	0	0	0	0
Lignin	0	0	319.15	0	0	0	319.15	0	0	908.35	908.35	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	28.813	0	0	0	28.813	0	0	0	0	0
Oth. sugar poly.	0	0	201.727	0	0	0	201.727	0	0	0	0	0
Others	0	0	0	260.5	0	0	0	0	0	260.5	260.5	260.24
Ash	0	0	23.477	0.024	0	0	23.477	0	0	0.024	0.024	0.023

Table A.3 : Aspen Plus simulation software mass flows for CS-1 (S27-S40).

Components	S28	S29	S30	S31	S32	S33	S34	S35	S36	S37	S38	S39	S40
Total flow	1816.7	1484.546	1271.69	359.707	911.983	908.35	3.633	33002.42	45695.72	45695.72	18278.29	27417.43	12225.78
Glucose	0	0.029	0.001	0.001	0	0	0	30.324	30.324	30.324	12.13	18.194	0
Xylose	0	0.443	0.019	0.019	0	0	0	461.506	461.506	461.506	184.602	276.903	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0.006	0	0	0	0	0	6.083	6.085	6.085	2.434	3.651	0
Oth. sugar mono.	0	0.319	0.014	0.014	0	0	0	332.915	332.915	332.915	133.166	199.75	0
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0	0	0
Ethanol	0	3.507	0.15	0.149	0.002	0	0.002	3657.019	12453.67	12453.67	4981.469	7472.203	4981.469
Water	1816.7	1479.732	363.134	359.502	3.631	0	3.631	27982.88	31807.17	31807.17	12722.87	19084.3	7193.134
Furfural	0	0.066	0.003	0.003	0	0	0	68.922	118.844	118.844	47.538	71.306	47.538
H_2SO_4	0	0.061	0.003	0.003	0	0	0	63.749	63.75	63.75	25.5	38.25	0
N_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	0	0.105	0.004	0.004	0	0	0	109.396	129.481	129.481	51.793	77.689	0.098
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0	0.028	0.001	0.001	0	0	0	29.1	31.448	31.448	12.579	18.869	3.546
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0	0	0
Lignin	0	0	908.35	0	908.35	908.35	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	0.25	0.011	0.011	0	0	0	260.5	260.5	260.5	104.2	156.3	0
Ash	0	0	0	0	0	0	0	0.023	0.023	0.023	0.009	0.014	0

Table A.4 : Aspen Plus simulation software mass flows for CS-1 (S41-S53).

Components	S41	S42	S43	S44	S45	S46	S47	S48	S49	S50	S51	S52	S53
Total flow	6052.502	17894.09	9523.337	25112.1	15575.84	15575.84	12.3	12.3	15696.11	15696.11	14873.35	822.752	7496.312
Glucose	12.13	0	18.194	0	30.324	30.324	0	0	30.324	30.324	0	30.324	0
Xylose	184.602	0	276.903	0	461.506	461.506	0	0	115.376	115.376	0	115.376	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	2.434	0	3.651	0	6.085	6.085	0	0	6.085	6.085	3.066	3.019	0
Oth. sugar mono.	133.166	0	199.75	0	332.915	332.915	0	0	332.915	332.915	0	332.915	0
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0	0	0
Ethanol	0	7472.203	0	12493.8	0	0	0	0	0	0	0	0	0
Water	5529.733	10348.01	8736.287	12612.09	14266.02	14266.02	12.3	12.3	14391.62	14391.62	14371.81	19.812	7151.759
Furfural	0	71.306	0	0	0	0	0	0	340.797	340.797	339.128	1.669	339.128
H_2SO_4	25.5	0	38.25	0	63.75	63.75	0	0	63.75	63.75	11.406	52.344	0
N_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	51.695	0.056	77.633	0.154	129.327	129.327	0	0	129.327	129.327	128.995	0.332	2.953
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	9.033	2.513	16.356	6.059	25.389	25.389	0	0	25.389	25.389	18.951	6.437	2.472
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0	0	0
Lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0	0	0
Others	104.2	0	156.3	0	260.5	260.5	0	0	260.5	260.5	0	260.5	0
Ash	0.009	0	0.014	0	0.023	0.023	0	0	0.023	0.023	0	0.023	0

Table A.5 : Aspen Plus simulation software mass flows for CS-1 (S54-S65).

Components	S54	S55	S56	S57	S58	S59	S60	S61	S62	S63	S64	S65
Total flow	7496.312	1324.271	1324.271	984.27	340	7156.312	7377.041	19433.17	4617.249	14371.61	4778.995	4778.995
Glucose	0	0	0	0	0	0	0	0	0	0	0	0
Xylose	0	0	0	0	0	0	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0	0	0	0	0	3.066	3.066	0	3.066	0	0
Oth. sugar mono.	0	0	0	0	0	0	0	0	0	0	0	0
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0	0
Ethanol	0	0	0	0	0	0	0	0	0	0	0	0
Water	7151.759	984.851	984.851	984.27	0.581	7151.178	7220.048	19271.05	0	14344.35	26.874	26.874
Furfural	339.128	339.126	339.126	0	339.126	0.002	0	0.002	0	0.001	0.002	0.002
H_2SO_4	0	0	0	0	0	0	11.406	11.406	0	11.406	0	0
N_2	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	2.953	0.008	0.008	0	0.008	2.944	126.042	128.986	0	9.519	119.467	119.467
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	2.472	0.285	0.285	0	0.285	2.187	16.479	18.666	0	3.263	15.403	15.403
Undecane	0	0	0	0	0	0	0	0	4617.249	0	4617.249	4617.249
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0	0
Lignin	0	0	0	0	0	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	0	0	0	0	0	0	0	0	0	0	0
Ash	0	0	0	0	0	0	0	0	0	0	0	0

Table A.6 : Aspen Plus simulation software mass flows for CS-1 (S66-S78).

Components	S66	S67	S68	S69	S70	S71	S72	S73	S74	S75	S76	S77	S78
Total flow	17.757	4761.238	17.757	14389.37	162.257	4598.981	4598.981	162.257	40.257	40.257	28.299	11.958	122
Glucose	0	0	0	0	0	0	0	0	0	0	0	0	0
Xylose	0	0	0	0	0	0	0	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0	0	3.066	0	0	0	0	0	0	0	0	0
Oth. sugar mono.	0	0	0	0	0	0	0	0	0	0	0	0	0
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0	0	0
Ethanol	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	16.582	10.292	16.582	14360.93	10.292	0	0	10.292	10.01	10.01	0	10.01	0.282
Furfural	0	0.002	0	0.001	0.002	0	0	0.002	0	0	0	0	0.001
H_2SO_4	0	0	0	11.406	0	0	0	0	0	0	0	0	0
N_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	0.732	118.735	0.732	10.252	114.337	4.398	4.398	114.337	0	0	0	0	114.337
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0.443	14.96	0.443	3.706	8.521	6.439	6.439	8.521	1.947	1.947	0	1.947	6.574
Undecane	0	4617.249	0	0	29.105	4588.144	4588.144	29.105	28.299	28.299	28.299	0	0.806
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0	0	0
Lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	0	0	0	0	0	0	0	0	0	0	0	0
Ash	0	0	0	0	0	0	0	0	0	0	0	0	0

Table A.7 : Aspen Plus simulation software mass flows for CS-1 (S79-S94).

Components	S79	S80	S81	S82	S83	S84	S85	S86	S87	S88	S89	S90	S91	S92	S93	S94
Total flow	122	804.651	18.101	0.905	17.196	0.53	1.435	0.816	0.269	110	110	110	11	99	13.52	12.111
Glucose	0	29.657	0.667	0.033	0.634	0.001	0.035	0	0	0	0	0	0	0	0	0
Xylose	0	112.838	2.538	0.127	2.411	0.001	0.128	0	0	0	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	2.953	0.066	0.003	0.063	0.001	0.004	0	0	0	0	0	0	0	0.004	0
Oth. sugar mono.	0	325.591	7.324	0.366	6.957	0.007	0.372	0	0	0	0	0	0	0	0	0
Sugar olig.	0	0	0	0	0	0.024	0.024	0	0	0	0	0	0	0	0.024	0
Ethanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	0.282	19.376	0.436	0.022	0.414	0.381	0.403	0	0	0	0	0	0	0	0.662	0.213
Furfural	0.001	1.632	0.037	0.002	0.035	0	0.002	0	0	0	0	0	0	0	0.002	0.001
H_2SO_4	0	51.192	1.152	0.058	1.094	0.012	0.07	0	0	0	0	0	0	0	0.07	0
N_2	0	0	0	0	0	0	0	0	0	86.9	86.9	86.9	8.69	78.21	8.69	8.69
CO_2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.466	0.466
O_2	0	0	0	0	0	0	0	0	0	23.1	23.1	23.1	2.31	20.79	1.982	1.982
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0.408	0	0	0	0	0	0	0.379	0.359
Acetic Acid	114.337	0.325	0.007	0	0.007	0.003	0.003	0	0	0	0	0	0	0	0.003	0.001
Glycerol	0	0	0	0	0	0.002	0.002	0	0	0	0	0	0	0	0.002	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0.269	0	0	0	0	0	0.269	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0.408	0	0	0	0	0	0	0.406	0.4
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	6.574	6.296	0.142	0.007	0.134	0.017	0.024	0	0	0	0	0	0	0	0.024	0
Undecane	0.806	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0.001	0.001	0	0	0	0	0	0	0	0.001	0
Lignin	0	0	0	0	0	0.002	0.002	0	0	0	0	0	0	0	0.002	0
Cellulase	0	0	0	0	0	0.007	0.007	0	0	0	0	0	0	0	0.007	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.17	0
ZYMO	0	0	0	0	0	0.005	0.005	0	0	0	0	0	0	0	0.005	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0.001	0.001	0	0	0	0	0	0	0	0	0
Others	0	254.769	5.731	0.287	5.444	0.064	0.351	0	0	0	0	0	0	0	0.351	0
Ash	0	0.023	0.001	0	0	0	0	0	0	0	0	0	0	0	0	0

Table A.8 : Aspen Plus simulation software mass flows for CS-1 (S95-S108).

Components	S95	S96	S97	S98	S99	S100	S101	S102	S103	S104	S105	S106	S107	S108
Total flow	1.409	8.16	10.2	23.612	33.812	12.138	131.989	131.989	149.184	303.703	108.136	120.247	195.568	39.114
Glucose	0	0	0	0	0	0	0.291	0.291	0.925	0	0	0	0	0
Xylose	0	0	0	0	0	0	0.318	0.318	2.729	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0.004	0	0	0	0	0	0.168	0.168	0.231	0.235	0	0	0.235	0.047
Oth. sugar mono.	0	0	0	0	0	0	1.567	1.567	8.524	0	0	0	0	0
Sugar olig.	0.024	0	0	0	0	0	5.949	5.949	5.949	5.973	0	0	5.973	1.194
Ethanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	0.449	0	0	0	0	0	94.936	94.936	95.351	102.146	1.831	2.045	100.314	20.063
Furfural	0.001	0	0	0	0	0	0.007	0.007	0.042	0.043	0.001	0.002	0.041	0.008
H_2SO_4	0.07	0	0	0	0	0	3.024	3.024	4.118	4.187	0	0	4.187	0.837
N_2	0	0	0	0	0	0	0	0	0	78.21	78.208	86.898	0.002	0
CO_2	0	0	0	0	0	0	0	0	0	11.715	11.703	12.169	0.012	0.002
O_2	0	0	0	0	0	0	0	0	0	12.449	12.449	14.431	0.001	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0.021	4.08	0	0	0	0	0	0	0	3.439	1.078	1.437	2.36	0.472
Acetic Acid	0.002	0	0	0	0	0	0.738	0.738	0.745	0.747	0.009	0.01	0.738	0.148
Glycerol	0.002	0	0	0	0	0	0.529	0.529	0.529	0.531	0	0	0.531	0.106
DAP	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0.269	0	0	23.612	23.612	0	0	0	0	23.881	0	0	23.881	4.776
Nutrients	0	0	10.2	0	10.2	0	0	0	0	10.2	0	0	10.2	2.04
SO_2	0.007	4.08	0	0	0	0	0	0	0	4.037	2.855	3.255	1.182	0.236
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0.024	0	0	0	0	0	4.228	4.228	4.363	4.388	0	0	4.388	0.877
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0.116	0.116	0.116	0	0	0	0	0
Xylan	0.001	0	0	0	0	0	0.186	0.186	0.186	0.187	0	0	0.187	0.037
Lignin	0.002	0	0	0	0	0	0.398	0.398	0.398	0.399	0	0	0.399	0.08
Cellulase	0.007	0	0	0	0	0	1.727	1.727	1.727	3.39	0	0	3.39	0.678
Biomass	0.17	0	0	0	0	0	0.05	0.05	0.05	2.023	0	0	2.023	0.405
ZYMO	0.005	0	0	0	0	0	1.353	1.353	1.353	1.359	0	0	1.359	0.272
Acetate	0	0	0	0	0	0	0.036	0.036	0.036	0.036	0	0	0.036	0.007
Oth. sugar poly.	0	0	0	0	0	0	0.25	0.25	0.25	0.079	0	0	0.079	0.016
Others	0.351	0	0	0	0	12.138	16.087	16.087	21.531	34.02	0	0	34.02	6.804
Ash	0	0	0	0	0	0	0.029	0.029	0.029	0.03	0	0	0.03	0.006

Table A.9 : Aspen Plus simulation software mass flows for CS-1 (S109-S121).

Components	S109	S110	S111	S112	S113	S114	S115	S116	S117	S118	S119	S120	S121
Total flow	156.454	3900.873	3900.873	467.187	4524.514	4524.514	16.749	1.105	4072.063	452.451	1.977	0.224	454.653
Glucose	0	29.657	29.657	0	1977.431	1977.431	0	0	1779.688	197.743	0	0	197.743
Xylose	0	112.838	112.838	0	112.838	112.838	0	0	101.554	11.284	0	0	11.284
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0.188	2.953	2.953	0	3.141	3.141	0	0	2.827	0.314	0	0	0.314
Oth. sugar mono.	0	325.591	325.591	0	325.591	325.591	0	0	293.032	32.559	0	0	32.559
Sugar olig.	4.779	0	0	0	106.191	106.191	0	0	95.571	10.619	0	0	10.619
Ethanol	0	46.328	46.328	0	46.328	46.328	0	0	41.695	4.633	0	0	4.633
Water	80.251	399.732	399.732	414.406	698.378	698.378	0	0	628.541	69.838	0	0	69.838
Furfural	0.033	1.895	1.895	0	1.928	1.928	0	0	1.735	0.193	0	0	0.193
H_2SO_4	3.35	51.192	51.192	0	54.542	54.542	0	0	49.088	5.454	0	0	5.454
N_2	0.001	0	0	0	0.001	0.001	0	0	0.001	0	0	0	0
CO_2	0.009	0	0	0	0.009	0.009	0	0	0.009	0.001	0	0	0.001
O_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	1.888	0	0	0	1.888	1.888	0	0	1.699	0.189	0	0	0.189
Acetic Acid	0.59	0.431	0.431	0	1.021	1.021	0	0	0.919	0.102	0	0	0.102
Glycerol	0.425	0	0	0	0.425	0.425	0	0	0.382	0.042	0	0	0.042
DAP	0	0	0	0	0	0	0	1.105	0	0	0	0.224	0.224
CSL	19.105	0	0	0	19.105	19.105	16.749	0	17.194	1.91	1.977	0	3.888
Nutrients	8.16	0	0	0	8.16	8.16	0	0	7.344	0.816	0	0	0.816
SO_2	0.945	0	0	0	0.945	0.945	0	0	0.851	0.095	0	0	0.095
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	3.509	6.308	6.308	0	9.816	9.816	0	0	8.836	0.982	0	0	0.982
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	1946.612	1946.612	0	93.437	93.437	0	0	84.094	9.344	0	0	9.344
Xylan	0.15	149.378	149.378	0	149.528	149.528	0	0	134.575	14.953	0	0	14.953
Lignin	0.319	319.15	319.15	0	319.469	319.469	0	0	287.523	31.947	0	0	31.947
Cellulase	2.712	0	0	52.781	55.492	55.492	0	0	49.943	5.549	0	0	5.549
Biomass	1.619	0	0	0	1.619	1.619	0	0	1.457	0.162	0	0	0.162
ZYMO	1.087	0	0	0	1.087	1.087	0	0	0.978	0.109	0	0	0.109
Acetate	0.029	28.813	28.813	0	28.842	28.842	0	0	25.958	2.884	0	0	2.884
Oth. sugar poly.	0.063	201.727	201.727	0	201.79	201.79	0	0	181.611	20.179	0	0	20.179
Others	27.217	254.769	254.769	0	281.986	281.986	0	0	253.787	28.198	0	0	28.198
Ash	0.024	23.5	23.5	0	23.523	23.523	0	0	21.171	2.352	0	0	2.352

Table A.10 : Aspen Plus simulation software mass flows for CS-1 (S122-S133).

Components	S122	S123	S124	S125	S126	S127	S128	S129	S130	S131	S132	S133
Total flow	454.653	118.24	336.414	4426.33	132.79	4293.54	132.79	4293.541	3328.159	1405.74	4733.9	1098.171
Glucose	6.526	0	6.526	1786.214	53.586	1732.627	0	5.198	5.198	0	5.198	0
Xylose	0.97	0	0.97	102.525	3.076	99.449	0	5.669	5.669	0	5.669	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0.314	0	0.314	3.141	0.094	3.046	0.094	3.046	3.141	0	3.141	0
Oth. sugar mono.	4.103	0	4.103	297.134	8.915	288.221	0	27.958	27.958	0	27.958	0
Sugar olig.	10.619	0	10.619	106.191	3.186	103.004	3.186	103.004	106.191	0	106.191	0
Ethanol	113.589	11.973	101.616	143.311	4.299	139.012	4.299	1149.35	1041.029	118.32	1159.349	112.621
Water	71.91	2.91	69	697.541	20.926	676.615	20.926	684.531	678.513	1284.702	1963.214	26.945
Furfural	0.193	0.003	0.189	1.925	0.058	1.867	0.058	1.867	1.895	0.033	1.928	0.03
H_2SO_4	5.454	0	5.454	54.542	1.636	52.906	1.636	52.906	54.542	0	54.542	0
N_2	0	0	0	0.001	0	0.001	0	0.001	0	0	0	0.001
CO_2	103.219	102.608	0.612	0.62	0.019	0.602	0.019	958.15	6.234	1.08	7.315	951.934
O_2	0.535	0.534	0	0.001	0	0.001	0	4.699	0.002	0	0.003	4.697
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0.189	0.099	0.09	1.789	0.054	1.736	0.054	1.736	0.872	0.898	1.77	0.918
Acetic Acid	3.682	0.05	3.632	4.551	0.137	4.414	0.137	35.831	35.508	0.51	36.018	0.46
Glycerol	0.986	0	0.986	1.368	0.041	1.327	0.041	9.602	9.643	0	9.643	0
DAP	0.097	0	0.097	1.202	0.036	1.166	0.036	0.612	0.648	0	0.648	0
CSL	3.434	0	3.434	37.377	1.121	36.256	1.121	34.282	35.404	0	35.404	0
Nutrients	0.816	0	0.816	8.16	0.245	7.915	0.245	7.915	8.16	0	8.16	0
SO_2	0.095	0.062	0.033	0.883	0.027	0.857	0.027	0.857	0.319	0.195	0.514	0.565
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	3.794	0	3.794	12.628	0.379	12.25	65.955	36.961	102.915	0.002	102.915	0.002
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	9.344	0	9.344	93.437	2.803	90.634	2.803	90.634	93.437	0	93.437	0
Xylan	14.953	0	14.953	149.528	4.486	145.042	4.486	145.042	149.528	0	149.528	0
Lignin	31.947	0	31.947	319.469	9.584	309.885	9.584	309.885	319.469	0	319.469	0
Cellulase	5.549	0	5.549	55.492	1.665	53.827	1.665	53.827	55.492	0	55.492	0
Biomass	0.162	0	0.162	1.619	0.049	1.57	0.049	1.57	1.619	0	1.619	0
ZYMO	8.034	0	8.034	9.012	0.27	8.742	0.27	43.204	43.474	0	43.474	0
Acetate	2.884	0	2.884	28.842	0.865	27.977	0.865	27.977	28.842	0	28.842	0
Oth. sugar poly.	20.179	0	20.179	201.79	6.054	195.736	6.054	195.736	201.79	0	201.79	0
Others	28.724	0	28.724	282.512	8.475	274.036	8.475	278.672	287.148	0	287.148	0
Ash	2.352	0	2.352	23.523	0.706	22.818	0.706	22.818	23.523	0	23.523	0

Table A.11 : Aspen Plus simulation software mass flows for CS-1 (S134-S145).

Components	S134	S135	S136	S137	S138	S139	S140	S141	S142	S143	S144	S145
Total flow	4733.9	4733.9	8	1581	3144.9	1224.411	1294.5	1113.17	1350	231	1350	1159.707
Glucose	5.198	5.198	0	0	5.198	0	0	0	0	0	0	0
Xylose	5.669	5.669	0	0	5.669	0	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	3.141	3.141	0	0.001	3.14	0	0	0	0	0.001	0	0
Oth. sugar mono.	27.958	27.958	0	0	27.958	0	0	0	0	0	0	0
Sugar olig.	106.191	106.191	0	0	106.191	0	0	0	0	0	0	0
Ethanol	1159.349	1159.349	1.077	1158.256	0.015	125.671	0	7.351	1158.256	0	1158.256	1155.94
Water	1963.214	1963.214	0.212	416.611	1546.391	30.067	1294.5	39.865	188.393	228.218	188.393	3.768
Furfural	1.928	1.928	0	0.461	1.467	0.033	0	0	0.461	0	0.461	0
H_2SO_4	54.542	54.542	0	0.001	54.541	0	0	0	0	0.001	0	0
N_2	0	0	0	0	0	0.001	0	0.001	0	0	0	0
CO_2	7.315	7.315	6.651	0.664	0	1061.193	0	1060.112	0.664	0	0.664	0
O_2	0.003	0.003	0.002	0	0	5.234	0	5.233	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	1.77	1.77	0.036	1.734	0	1.053	0	0.155	1.734	0	1.734	0
Acetic Acid	36.018	36.018	0	2.73	33.288	0.51	0	0	0	2.73	0	0
Glycerol	9.643	9.643	0	0	9.643	0	0	0	0	0	0	0
DAP	0.648	0.648	0	0	0.648	0	0	0	0	0	0	0
CSL	35.404	35.404	0	0	35.404	0	0	0	0	0	0	0
Nutrients	8.16	8.16	0	0	8.16	0	0	0	0	0	0	0
SO_2	0.514	0.514	0.021	0.493	0	0.648	0	0.453	0.493	0	0.493	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	102.915	102.915	0	0.049	102.866	0.002	0	0	0	0.049	0	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	93.437	93.437	0	0	93.437	0	0	0	0	0	0	0
Xylan	149.528	149.528	0	0	149.528	0	0	0	0	0	0	0
Lignin	319.469	319.469	0	0	319.469	0	0	0	0	0	0	0
Cellulase	55.492	55.492	0	0	55.492	0	0	0	0	0	0	0
Biomass	1.619	1.619	0	0	1.619	0	0	0	0	0	0	0
ZYMO	43.474	43.474	0	0	43.474	0	0	0	0	0	0	0
Acetate	28.842	28.842	0	0	28.842	0	0	0	0	0	0	0
Oth. sugar poly.	201.79	201.79	0	0	201.79	0	0	0	0	0	0	0
Others	287.148	287.148	0	0	287.148	0	0	0	0	0	0	0
Ash	23.523	23.523	0	0	23.523	0	0	0	0	0	0	0

Table A.12 : Aspen Plus simulation software mass flows for CS-1 (S146-S157).

Components	S146	S147	S148	S149	S150	S151	S152	S153	S154	S155	S156	S157
Total flow	190.293	1159.707	190.293	3144.9	1576.065	1576.065	1568.835	1568.835	608.298	960.536	152.075	147
Glucose	0	0	0	5.198	0	0	5.198	5.198	4.678	0.52	1.17	0
Xylose	0	0	0	5.669	0	0	5.669	5.669	5.102	0.567	1.275	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0	0	3.14	0.152	0.152	2.988	2.988	2.689	0.299	0.672	0
Oth. sugar mono.	0	0	0	27.958	0	0	27.958	27.958	25.162	2.795	6.29	0
Sugar olig.	0	0	0	106.191	0	0	106.191	106.191	95.571	10.619	23.893	0
Ethanol	2.317	1155.94	2.317	0.015	0.015	0.015	0	0	0	0	0	0
Water	184.625	3.768	184.625	1546.391	1519.491	1519.491	26.9	26.9	24.21	2.69	6.053	147
Furfural	0.461	0	0.461	1.467	1.347	1.347	0.12	0.12	0.108	0.012	0.027	0
H_2SO_4	0	0	0	54.541	0.576	0.576	53.966	53.966	48.569	5.397	12.142	0
N_2	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0.664	0	0.664	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	1.734	0	1.734	0	0	0	0	0	0	0	0	0
Acetic Acid	0	0	0	33.288	32.255	32.255	1.033	1.033	0.93	0.103	0.232	0
Glycerol	0	0	0	9.643	0.2	0.2	9.443	9.443	8.498	0.944	2.125	0
DAP	0	0	0	0.648	0	0	0.648	0.648	0	0.648	0	0
CSL	0	0	0	35.404	0	0	35.404	35.404	0	35.404	0	0
Nutrients	0	0	0	8.16	0	0	8.16	8.16	0	8.16	0	0
SO_2	0.493	0	0.493	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0	0	0	102.866	22.022	22.022	80.844	80.844	67.732	13.112	16.933	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	93.437	0	0	93.437	93.437	1.869	91.569	0.467	0
Xylan	0	0	0	149.528	0	0	149.528	149.528	2.991	146.537	0.748	0
Lignin	0	0	0	319.469	0	0	319.469	319.469	6.389	313.08	1.597	0
Cellulase	0	0	0	55.492	0	0	55.492	55.492	27.746	27.746	6.937	0
Biomass	0	0	0	1.619	0	0	1.619	1.619	0.809	0.809	0.202	0
ZYMO	0	0	0	43.474	0	0	43.474	43.474	21.737	21.737	5.434	0
Acetate	0	0	0	28.842	0	0	28.842	28.842	0.577	28.265	0.144	0
Oth. sugar poly.	0	0	0	201.79	0	0	201.79	201.79	4.036	197.754	1.009	0
Others	0	0	0	287.148	0.008	0.008	287.139	287.139	258.426	28.714	64.606	0
Ash	0	0	0	23.523	0	0	23.523	23.523	0.47	23.053	0.117	0

Table A.13 : Aspen Plus simulation software mass flows for CS-1 (S158-S170).

Components	S158	S159	S160	S161	S162	S163	S164	S165	S166	S167	S168	S169	S170
Total flow	456.224	1655.174	30.914	30.914	30.914	31.176	960.274	1144.347	50.608	405.616	50.608	28.501	377.115
Glucose	3.509	0	0	0	0	0	0.52	0	0	3.509	0	0	3.509
Xylose	3.826	0.002	0	0	0	0	0.567	0	0	3.826	0	0.002	3.824
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	2.017	1.523	0	0	0	0	0.299	0	0.671	1.346	0.671	0.7	0.646
Oth. sugar mono.	18.872	0.006	0	0	0	0	2.795	0	0	18.872	0	0.006	18.865
Sugar olig.	71.679	0	0	0	0	0	10.619	0	0	71.679	0	0	71.678
Ethanol	0	0.015	0	0	0	0	0	7.351	0	0	0	0	0
Water	18.158	1537.636	0	0	0	0.256	2.434	40.121	17.676	0.482	17.676	0.469	0.013
Furfural	0.081	1.427	0	0	0	0	0.012	0	0.071	0.01	0.071	0.009	0.001
H_2SO_4	36.427	20.074	0	0	0	0	5.397	0	6.149	30.278	6.149	13.349	16.929
N_2	0	0	24.422	24.422	24.422	24.421	0.001	24.423	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	1060.112	0	0	0	0	0
O_2	0	0	6.492	6.492	6.492	6.492	0	11.725	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0.155	0	0	0	0	0
Acetic Acid	0.697	32.95	0	0	0	0.006	0.097	0.006	0.662	0.035	0.662	0.034	0.002
Glycerol	6.374	3.085	0	0	0	0	0.944	0	1.146	5.227	1.146	1.739	3.489
DAP	0	0	0	0	0	0	0.648	0	0	0	0	0	0
CSL	0	0	0	0	0	0	35.404	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	8.16	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0.453	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	50.799	57.858	0	0	0	0.001	13.112	0.001	24.088	26.71	24.088	11.748	14.962
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	1.402	0	0	0	0	0	91.569	0	0	1.402	0	0	1.402
Xylan	2.243	0	0	0	0	0	146.537	0	0	2.243	0	0	2.243
Lignin	4.792	0	0	0	0	0	313.08	0	0	4.792	0	0	4.792
Cellulase	20.81	0	0	0	0	0	27.746	0	0	20.81	0	0	20.81
Biomass	0.607	0	0	0	0	0	0.809	0	0	0.607	0	0	0.607
ZYMO	16.303	0	0	0	0	0	21.737	0	0	16.303	0	0	16.303
Acetate	0.433	0	0	0	0	0	28.265	0	0	0.433	0	0	0.433
Oth. sugar poly.	3.027	0	0	0	0	0	197.754	0	0	3.027	0	0	3.027
Others	193.82	0.599	0	0	0	0	28.714	0	0.145	193.675	0.145	0.446	193.229
Ash	0.352	0	0	0	0	0	23.053	0	0	0.352	0	0	0.352

Table A.14 : Aspen Plus simulation software mass flows for CS-1 (S171-S184).

Components	S171	S173	S174	S175	S176	S177	S178	S179	S180	S181	S182	S183	S184
Total flow	1337.389	28.501	530.075	397.556	2243.023	1065.3	17697.69	17697.69	7.522	17705.21	17705.21	194.088	17511.12
Glucose	4.028	0	1.17	0.877	0.877	0.04	0.917	0.917	0	0.917	0.064	0	0.064
Xylose	4.391	0.002	1.275	0.957	0.959	0.044	1.003	1.003	0	1.003	0.07	0	0.07
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0.944	0.7	0.673	0.505	2.028	0.009	5.103	5.103	0	5.103	0.357	0	0.357
Oth. sugar mono.	21.661	0.006	6.29	4.718	4.724	0.217	4.94	4.94	0	4.94	0.346	0	0.346
Sugar olig.	82.297	0	23.893	17.92	17.92	0.823	18.743	18.743	0	18.743	1.312	0	1.312
Ethanol	0	0	0	0	2.332	0	2.332	2.332	0	2.332	0.163	0.001	0.162
Water	2.447	0.469	381.271	285.953	2008.214	1060.6	17429.75	17429.75	0	17429.75	17428.67	6.204	17422.46
Furfural	0.013	0.009	0.027	0.02	1.908	0	1.908	1.908	0	1.908	0.134	0.001	0.133
H_2SO_4	22.325	13.349	12.143	9.107	29.181	0.004	40.591	40.591	0	40.591	40.591	0	40.591
N_2	0.001	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0.664	0	0.664	0.664	0	0.664	158.701	147.718	10.983
O_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	40.225	40.091	0.135
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	1.734	0	1.734	1.734	0	1.734	6.005	0.043	5.962
Acetic Acid	0.099	0.034	2.963	2.222	35.172	0	45.424	45.424	0	45.424	3.18	0.001	3.179
Glycerol	4.433	1.739	2.125	1.594	4.679	0.044	4.723	4.723	0	4.723	0.331	0	0.331
DAP	0.648	0	0	0	0	0.65	0.65	0.65	0	0.65	0.65	0	0.65
CSL	35.404	0	0	0	0	0.354	0.354	0.354	0	0.354	0.354	0	0.354
Nutrients	8.16	0	0	0	0	0	0	0	7.522	7.522	7.522	0	7.522
SO_2	0	0	0	0	0.493	0	0.493	0.493	0	0.493	0.493	0.017	0.476
H_2S	0	0	0	0	0	0	0	0	0	0	0.091	0.013	0.078
Oth. inorg.acids	28.075	11.748	16.982	12.737	70.595	0.272	74.572	74.572	0	74.572	5.22	0	5.22
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	92.97	0	0.467	0.35	0.35	0	0.35	0.35	0	0.35	0.025	0	0.025
Xylan	148.78	0	0.748	0.561	0.561	0	0.561	0.561	0	0.561	0.039	0	0.039
Lignin	317.872	0	1.597	1.198	1.198	0	1.198	1.198	0	1.198	0.084	0	0.084
Cellulase	48.556	0	6.937	5.202	5.202	0	5.202	5.202	0	5.202	0.364	0	0.364
Biomass	1.416	0	0.202	0.152	0.152	0	0.152	0.152	0	0.152	6.175	0	6.175
ZYMO	38.04	0	5.434	4.076	4.076	0	4.076	4.076	0	4.076	0.285	0	0.285
Acetate	28.698	0	0.144	0.108	0.108	0	0.108	0.108	0	0.108	0.008	0	0.008
Oth. sugar poly.	200.781	0	1.009	0.756	0.756	0	0.756	0.756	0	0.756	0.053	0	0.053
Others	221.942	0.446	64.606	48.454	49.053	2.22	51.273	51.273	0	51.273	3.589	0	3.589
Ash	23.406	0	0.117	0.088	0.088	0.023	0.111	0.111	0	0.111	0.111	0	0.111

Table A.15 : Aspen Plus simulation software mass flows for CS-1 (S185-S197).

Components	S185	S186	S187	S188	S189	S190	S191	S192	S193	S194	S195	S196	S197
Total flow	0.033	6733.64	24253	6856.657	7050.745	17396.34	252.339	17144	126.199	126.14	63.129	63.07	8.207
Glucose	0	0	0.006	0	0	0.006	0	0.006	0	0	0	0	0
Xylose	0	0	0.007	0	0	0.007	0	0.007	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0	0.036	0	0	0.036	0	0.035	0	0	0	0	0
Oth. sugar mono.	0	0	0.035	0	0	0.035	0	0.034	0	0	0	0	0
Sugar olig.	0	0	0.131	0	0	0.131	0.001	0.129	0.001	0.001	0	0	0
Ethanol	0	0	0.016	0.002	0.003	0.014	0	0.014	0	0	0	0	0
Water	0	0	17433.36	106.935	113.14	17326.43	238.876	17087.55	113.151	125.725	50.289	62.862	6.538
Furfural	0	0	0.013	0.001	0.002	0.012	0	0.012	0	0	0	0	0
H_2SO_4	0	0	40.606	0	0	40.606	0.56	40.046	0.265	0.295	0.118	0.147	0.015
N_2	0	5319.576	5319.635	5319.369	5319.369	0.266	0.004	0.262	0.002	0.002	0.001	0.001	0
CO_2	0	0	23.196	23.133	170.851	0.063	0.001	0.062	0	0	0	0	0
O_2	0	1414.064	1406.355	1406.217	1406.217	0.138	0.002	0.136	0.001	0.001	0	0.001	0
CH_4	0	0	0.135	0.135	40.225	0	0	0	0	0	0	0	0
NO_x	0	0	0.345	0.069	0.069	0.276	0.004	0.272	0.002	0.002	0.001	0.001	0
NH_3	0	0	5.964	0.507	0.55	5.457	0.075	5.382	0.036	0.04	0.016	0.02	0.002
Acetic Acid	0	0	0.318	0.001	0.002	0.317	0.004	0.312	0.002	0.002	0.001	0.001	0
Glycerol	0	0	0.033	0	0	0.033	0	0.033	0	0	0	0	0
DAP	0	0	0.65	0	0	0.65	0.009	0.641	0.004	0.005	0.002	0.002	0
CSL	0	0	0.354	0	0	0.354	0.005	0.349	0.002	0.003	0.001	0.001	0
Nutrients	0.033	0	7.558	0	0	7.558	0.104	7.454	0.049	0.055	0.022	0.027	0.003
SO_2	0	0	0.484	0.224	0.241	0.26	0.004	0.256	0.002	0.002	0.001	0.001	0
H_2S	0	0	0.078	0.064	0.077	0.014	0	0.014	0	0	0	0	0
Oth. inorg.acids	0	0	0.523	0	0	0.522	0.007	0.514	0.003	0.003	0.001	0.002	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0.002	0	0	0.002	0.002	0	0.002	0	0.002	0	0
Xylan	0	0	0.004	0	0	0.004	0.004	0	0.004	0	0.004	0	0.001
Lignin	0	0	0.008	0	0	0.008	0.008	0	0.008	0	0.008	0	0.001
Cellulase	0	0	0.037	0	0	0.037	0.037	0	0.037	0	0.037	0	0.005
Biomass	0	0	12.485	0	0	12.485	12.485	0	12.485	0	12.485	0	1.623
ZYMO	0	0	0.029	0	0	0.029	0.029	0	0.029	0	0.029	0	0.004
Acetate	0	0	0.001	0	0	0.001	0.001	0	0.001	0	0.001	0	0
Oth. sugar poly.	0	0	0.006	0	0	0.006	0.006	0	0.006	0	0.006	0	0
Others	0	0	0.46	0	0	0.46	0.007	0.453	0.003	0.003	0.001	0.001	0
Ash	0	0	0.124	0	0	0.124	0.101	0.023	0.101	0	0.101	0	0.013

Table A.16 : Aspen Plus simulation software mass flows for CS-1 (S198-S210).

Components	S198	S199	S200	S201	S202	S203	S204	S205	S206	S207	S208	S209	S210
Total flow	54.922	22.945	31.977	22.945	17356.16	8497.232	17152.35	500	4919.592	500	5419.592	22536.21	35.734
Glucose	0	0	0	0	0.006	4.028	0.04	0	0	0	0	0.04	0
Xylose	0	0	0	0	0.007	4.391	0.044	0	0	0	0	0.044	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0	0	0	0.036	0.945	0.009	0	0	0	0	0.009	0
Oth. sugar mono.	0	0	0	0	0.034	21.661	0.217	0	0	0	0	0.217	0
Sugar olig.	0	0	0	0	0.13	82.298	0.823	0	0	0	0	0.823	0
Ethanol	0	0	0	0	0.014	0.003	0	0	0	0	0	0	0
Water	43.751	22.929	20.822	22.929	17299.07	146.419	976.332	89.777	0	89.777	89.777	1066.109	0
Furfural	0	0	0	0	0.012	0.015	0	0	0	0	0	0	0
H_2SO_4	0.103	0	0.103	0	40.488	22.428	0.004	0	0	0	0	0.004	0
N_2	0.001	0.001	0	0.001	0.266	5319.37	12182.3	0	3886.478	0	3886.478	16068.78	0
CO_2	0	0	0	0	0.063	170.851	2625.953	0	0	0	990.742	3616.695	0
O_2	0	0	0	0	0.138	1406.218	1312.072	133.802	1033.114	133.802	446.564	1758.636	0
CH_4	0	0	0	0	0	40.225	0.402	0	0	0	0	0.402	0
NO_x	0.001	0.001	0	0.001	0.276	0.069	1.086	2.959	0	2.959	2.959	4.045	0
NH_3	0.014	0.013	0.001	0.013	5.454	0.551	0	0	0	0	0	0	0
Acetic Acid	0.001	0	0	0	0.316	0.102	0.001	0	0	0	0	0.001	0
Glycerol	0	0	0	0	0.033	4.433	0.044	0	0	0	0	0.044	0
DAP	0.002	0	0.002	0	0.648	0.65	0.65	0	0	0	0	0.65	0
CSL	0.001	0	0.001	0	0.353	35.405	0.354	0	0	0	0	0.354	0
Nutrients	0.019	0	0.019	0	7.536	8.179	0	0	0	0	0	0	0
SO_2	0.001	0.001	0	0.001	0.26	0.241	16.472	0	0	0	0	16.472	0
H_2S	0	0	0	0	0.014	0.077	0	0.341	0	0.341	0.341	0.341	0
Oth. inorg.acids	0.001	0	0.001	0	0.521	30.023	0.3	0	0	0	0	0.3	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0.002	0	0.002	0	0	92.972	0.93	0	0	0	0	0	0.93
Xylan	0.003	0	0.003	0	0	148.784	1.488	0	0	0	0	0	1.488
Lignin	0.007	0	0.007	0	0	317.88	3.179	0	0	0	0	0	3.179
Cellulase	0.032	0	0.032	0	0	48.588	0.486	0	0	0	0	0	0.486
Biomass	10.862	0	10.862	0	0	12.279	0.123	0	0	0	0	0	0.123
ZYMO	0.025	0	0.025	0	0	38.065	0.381	0	0	0	0	0	0.381
Acetate	0.001	0	0.001	0	0	28.698	0.287	0	0	0	0	0	0.287
Oth. sugar poly.	0.004	0	0.004	0	0	200.785	2.008	0	0	0	0	0	2.008
Others	0.001	0	0.001	0	0.459	287.107	2.872	273.121	0	273.121	2.731	2.22	3.383
Ash	0.088	0	0.088	0	0.023	23.494	23.494	0	0	0	0	0.023	23.471

Table A.17 : Aspen Plus simulation software mass flows for CS-1 (S211-S224).

Components	S211	S212	S213	S214	S215	S216	S217	S218	S219 – S224
Total flow	22536.21	8655.119	8655.119	22536.21	21475.62	1060.59	21470.91	4.71	13688.83
Glucose	0.04	0	0	0.04	0.04	0	0	0.04	0
Xylose	0.044	0	0	0.044	0.044	0	0	0.044	0
Soluble lignin	0	0	0	0	0	0	0	0	0
HMF	0.009	0	0	0.009	0.009	0	0	0.009	0
Oth. sugar mono.	0.217	0	0	0.217	0.217	0	0	0.217	0
Sugar olig.	0.823	0	0	0.823	0.823	0	0	0.823	0
Ethanol	0	0	0	0	0	0	0	0	0
Water	1066.109	0	0	1066.109	5.519	1060.59	5.509	0.01	13688.83
Furfural	0	0	0	0	0	0	0	0	0
H_2SO_4	0.004	0	0	0.004	0.004	0	0	0.004	0
N_2	16068.78	6837.544	6837.544	16068.78	16068.78	0	16068.78	0	0
CO_2	3616.695	0	0	3616.695	3616.695	0	3616.695	0	0
O_2	1758.636	1817.575	1817.575	1758.636	1758.636	0	1758.636	0	0
CH_4	0.402	0	0	0.402	0.402	0	0.402	0	0
NO_x	4.045	0	0	4.045	4.045	0	4.045	0	0
NH_3	0	0	0	0	0	0	0	0	0
Acetic Acid	0.001	0	0	0.001	0.001	0	0.001	0	0
Glycerol	0.044	0	0	0.044	0.044	0	0	0.044	0
DAP	0.65	0	0	0.65	0.65	0	0	0.65	0
CSL	0.354	0	0	0.354	0.354	0	0	0.354	0
Nutrients	0	0	0	0	0	0	0	0	0
SO_2	16.472	0	0	16.472	16.472	0	16.471	0	0
H_2S	0.341	0	0	0.341	0.341	0	0.341	0	0
Oth. inorg.acids	0.3	0	0	0.3	0.3	0	0.028	0.272	0
Undecane	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0
Lignin	0	0	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0
Others	2.22	0	0	2.22	2.22	0	0	2.22	0
Ash	0.023	0	0	0.023	0.023	0	0	0.023	0

Table A.18 : Aspen Plus simulation software mass flows for CS-2 (S1-S12).

Components	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
Total flow	45.56	5000	63.75	30241.95	30241.95	30241.95	30241.95	27627.72	2614.23	27627.72	27627.72	68.362
Glucose	0	0	0	0	0	0	9.813	9.813	0	9.813	29.438	0
Xylose	0	0	0	0	0	0	203.774	203.774	0	203.774	486.956	0
Soluble lignin	0	0	0	0	0	0	894.364	894.364	0	894.364	894.364	0
HMF	0	0	0	0	0	0	9.088	9.088	0	9.088	5.907	0
Oth. sugar mono.	0	0	0	0	0	0	243.552	243.552	0	243.552	387.123	0
Sugar olig.	0	0	0	0	0	0	396.078	396.078	0	396.078	0	0
Ethanol	5.69	0	0	12500	12500	12500	12500	12500	0	12500	12500	0
Water	39.87	30.9	0	12709.1	12709.1	12709.1	12697.95	12697.95	0	12697.95	12646.29	0
Furfural	0	0	0	0	0	0	125.675	125.675	0	125.675	125.675	0
H_2SO_4	0	0	63.75	63.75	63.75	63.75	63.75	63.75	0	63.75	63.75	0
N_2	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	0	0	0	0	0	0	64.794	64.794	0	64.794	145.785	0
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0	0	0	0	0	0	29.888	29.888	0	29.888	29.888	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	1947.4	0	1947.4	1947.4	1947.4	1889.747	0	1889.747	0	0	0
Xylan	0	815.1	0	815.1	815.1	815.1	157.616	0	157.616	0	0	0
Lignin	0	1208.6	0	1208.6	1208.6	1208.6	314.236	0	314.236	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	178.2	0	178.2	178.2	178.2	32.415	0	32.415	0	0	0
Oth. sugar poly.	0	540.2	0	540.2	540.2	540.2	184.802	0	184.802	0	0	0
Others	0	244.15	0	244.15	244.15	244.15	307.968	307.968	0	307.968	312.512	68.362
Ash	0	35.45	0	35.45	35.45	35.45	35.415	0	35.415	0	0	0

Table A.19 : Aspen Plus simulation software mass flows for CS-2 (S13-S23).

Components	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23
Total flow	27559.36	13320.11	13320.11	12669.95	3264.392	14239.25	391.222	391.222	3032.507	623.107	17508.11
Glucose	29.438	0	0	0	0	29.438	0	0	0	0	0
Xylose	486.956	0	0	0	0	486.956	0	0	0	0	0
Soluble lignin	894.364	0	0	0	0	894.364	0	0	0	0	0
HMF	5.907	0.002	0.002	0.002	0	5.905	0	0	0	0	0
Oth. sugar mono.	387.123	0	0	0	0	387.123	0	0	0	0	0
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0
Ethanol	12500	9231.646	9231.646	8781.044	450.602	3268.354	0	0	45.561	405.04	0
Water	12646.29	4007.56	4007.56	3811.949	195.611	8638.726	391.222	391.222	372.316	214.518	17508.11
Furfural	125.675	54.938	54.938	52.256	2.682	70.737	0	0	0.271	2.41	0
H_2SO_4	63.75	0.001	0.001	0.001	0	63.749	0	0	0	0	0
N_2	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	145.785	23.626	23.626	22.473	1.153	122.159	0	0	0.117	1.037	0
Glycerol	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	29.888	2.334	2.334	2.219	0.114	27.554	0	0	0.011	0.102	0
Undecane	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	1889.747	0	0	0	1889.747	0	0
Xylan	0	0	0	0	157.616	0	0	0	157.616	0	0
Lignin	0	0	0	0	314.236	0	0	0	314.236	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	32.415	0	0	0	32.415	0	0
Oth. sugar poly.	0	0	0	0	184.802	0	0	0	184.802	0	0
Others	244.15	0	0	0	0	244.15	0	0	0	0	0
Ash	0	0	0	0	35.415	0	0	0	35.415	0	0

Table A.20 : Aspen Plus simulation software mass flows for CS-2 (S24-S35).

Components	S24	S25	S26	S27	S28	S29	S30	S31	S32	S33	S34	S35
Total flow	31747.36	32370.47	31444.63	925.84	1788.728	1462.459	1252.11	354.168	897.941	894.364	3.577	33264.83
Glucose	29.438	29.438	29.409	0.029	0	0.028	0.001	0.001	0	0	0	29.438
Xylose	486.956	486.956	486.469	0.487	0	0.467	0.02	0.019	0	0	0	486.956
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	5.905	5.905	5.899	0.006	0	0.006	0	0	0	0	0	5.905
Oth. sugar mono.	387.123	387.123	386.736	0.386	0	0.371	0.015	0.015	0	0	0	387.123
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0	0
Ethanol	3268.354	3673.394	3669.721	3.673	0	3.526	0.148	0.146	0.001	0	0.001	3673.394
Water	26146.83	26361.35	26334.99	26.361	1788.728	1457.549	357.54	353.964	3.575	0	3.575	28150.08
Furfural	70.737	73.148	73.075	0.073	0	0.07	0.003	0.003	0	0	0	73.148
H_2SO_4	63.749	63.749	63.686	0.064	0	0.061	0.003	0.003	0	0	0	63.749
N_2	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	122.159	123.196	123.072	0.123	0	0.118	0.005	0.005	0	0	0	123.196
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	27.554	27.656	27.629	0.027	0	0.027	0.001	0.001	0	0	0	27.656
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0	0
Lignin	894.364	894.364	0	894.364	0	0	894.364	0	894.364	894.364	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0	0
Others	244.15	244.15	243.906	0.244	0	0.234	0.01	0.01	0	0	0	244.15
Ash	0	0	0	0	0	0	0	0	0	0	0	0

Table A.21 : Aspen Plus simulation software mass flows for CS-2 (S36-S46).

Components	S36	S37	S38	S39	S40	S41	S42	S43	S44	S45	S46
Total flow	45934.78	45934.78	18373.91	27560.87	12269.16	6104.753	17957.24	9603.626	25132.64	15708.38	15708.38
Glucose	29.438	29.438	11.775	17.663	0	11.775	0	17.663	0	29.438	29.438
Xylose	486.956	486.956	194.782	292.173	0	194.782	0	292.173	0	486.956	486.956
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0
HMF	5.907	5.907	2.363	3.544	0	2.363	0	3.544	0	5.907	5.907
Oth. sugar mono.	387.123	387.123	154.849	232.274	0	154.849	0	232.274	0	387.123	387.123
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0
Ethanol	12454.44	12454.44	4981.775	7472.663	4981.775	0	7472.663	0	12494.31	0	0
Water	31962.03	31962.03	12784.81	19177.22	7233.741	5551.071	10406.88	8770.337	12632.4	14321.41	14321.41
Furfural	125.404	125.404	50.162	75.242	50.162	0	75.242	0	0	0	0
H_2SO_4	63.75	63.75	25.5	38.25	0	25.5	0	38.25	0	63.75	63.75
N_2	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	145.669	145.669	58.268	87.401	0.11	58.157	0.063	87.338	0.173	145.495	145.495
Glycerol	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	29.876	29.876	11.951	17.925	3.369	8.582	2.39	15.536	5.759	24.118	24.118
Undecane	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0
Lignin	0	0	0	0	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0
Others	244.15	244.15	97.66	146.49	0	97.66	0	146.49	0	244.15	244.15
Ash	0	0	0	0	0	0	0	0	0	0	0

Table A.22 : Aspen Plus simulation software mass flows for CS-2 (S47-S58).

Components	S47	S48	S49	S50	S51	S52	S53	S54	S55	S56	S57	S58
Total flow	11.45	11.45	15834.55	15834.55	14967.91	866.638	7546.54	7546.54	1330.169	1330.169	972.17	358
Glucose	0	0	29.438	29.438	0	29.438	0	0	0	0	0	0
Xylose	0	0	121.739	121.739	0	121.739	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0	5.907	5.907	2.947	2.96	0	0	0	0	0	0
Oth. sugar mono.	0	0	387.123	387.123	0	387.123	0	0	0	0	0	0
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0	0
Ethanol	0	0	0	0	0	0	0	0	0	0	0	0
Water	11.45	11.45	14453.88	14453.88	14433.6	20.287	7183.76	7183.76	972.782	972.782	972.17	0.613
Furfural	0	0	358.911	358.911	357.116	1.796	357.116	357.116	357.113	357.113	0	357.113
H_2SO_4	0	0	63.75	63.75	11.223	52.527	0	0	0	0	0	0
N_2	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	0	0	145.495	145.495	145.114	0.381	3.317	3.317	0.009	0.009	0	0.009
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0	0	24.118	24.118	17.916	6.201	2.347	2.347	0.265	0.265	0	0.265
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0	0
Lignin	0	0	0	0	0	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	0	244.15	244.15	0	244.15	0	0	0	0	0	0
Ash	0	0	0	0	0	0	0	0	0	0	0	0

Table A.23 : Aspen Plus simulation software mass flows for CS-2 (S59-S69).

Components	S59	S60	S61	S62	S63	S64	S65	S66	S67	S68	S69
Total flow	7188.54	7421.371	19588.95	5194.23	14433.96	5370.186	5370.186	17.899	5352.287	17.899	14451.85
Glucose	0	0	0	0	0	0	0	0	0	0	0
Xylose	0	0	0	0	0	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0
HMF	0	2.947	2.947	0	2.947	0	0	0	0	0	2.947
Oth. sugar mono.	0	0	0	0	0	0	0	0	0	0	0
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0
Ethanol	0	0	0	0	0	0	0	0	0	0	0
Water	7183.148	7249.834	19412.02	0	14405.99	26.99	26.99	16.653	10.337	16.653	14422.65
Furfural	0.003	0	0.003	0	0.001	0.002	0.002	0	0.002	0	0.001
H_2SO_4	0	11.223	11.223	0	11.223	0	0	0	0	0	11.223
N_2	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	3.308	141.797	145.105	0	10.709	134.396	134.396	0.824	133.572	0.824	11.533
Glycerol	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	2.082	15.569	17.652	0	3.083	14.568	14.568	0.421	14.146	0.421	3.505
Undecane	0	0	0	5194.23	0	5194.23	5194.23	0	5194.23	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0
Lignin	0	0	0	0	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0
Others	0	0	0	0	0	0	0	0	0	0	0
Ash	0	0	0	0	0	0	0	0	0	0	0

Table A.24 : Aspen Plus simulation software mass flows for CS-2 (S70-S82).

Components	S70	S71	S72	S73	S74	S75	S76	S77	S78	S79	S80	S81	S82
Total flow	179.769	5172.518	5172.518	179.769	61.769	61.769	32.728	29.042	118	118	847.572	19.066	0.953
Glucose	0	0	0	0	0	0	0	0	0	0	28.79	0.648	0.032
Xylose	0	0	0	0	0	0	0	0	0	0	119.061	2.678	0.134
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0	0	0	0	0	0	0	0	0	2.895	0.065	0.003
Oth. sugar mono.	0	0	0	0	0	0	0	0	0	0	378.606	8.517	0.425
Sugar olig.	0	0	0	0	0	0	0	0	0	0	0	0	0
Ethanol	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	10.337	0	0	10.337	10.332	10.332	0	10.332	0.005	0.005	19.841	0.446	0.022
Furfural	0.002	0	0	0.002	0	0	0	0	0.002	0.002	1.756	0.04	0.002
H_2SO_4	0	0	0	0	0	0	0	0	0	0	51.371	1.156	0.058
N_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	128.625	4.948	4.948	128.625	16.732	16.732	0	16.732	111.893	111.893	0.373	0.008	0
Glycerol	0	0	0	0	0	0	0	0	0	0	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0	0	0	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	8.064	6.083	6.083	8.064	1.978	1.978	0	1.978	6.086	6.086	6.065	0.136	0.007
Undecane	32.742	5161.488	5161.488	32.742	32.728	32.728	32.728	0	0.015	0.015	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0	0	0
Lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	0	0	0	0	0	0	0	0	0	238.779	5.371	0.269
Ash	0	0	0	0	0	0	0	0	0	0	0	0	0

Table A.25 : Aspen Plus simulation software mass flows for CS-2 (S83-S98).

Components	S83	S84	S85	S86	S87	S88	S89	S90	S91	S92	S93	S94	S95	S96	S97	S98
Total flow	18.113	0.525	1.478	0.816	0.007	110	110	110	11	99	13.301	12.139	1.162	8.16	10.2	23.612
Glucose	0.615	0.001	0.034	0	0	0	0	0	0	0	0	0	0	0	0	0
Xylose	2.544	0.001	0.135	0	0	0	0	0	0	0	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0.062	0.001	0.004	0	0	0	0	0	0	0	0.004	0	0.004	0	0	0
Oth. sugar mono.	8.09	0.007	0.434	0	0	0	0	0	0	0	0	0	0	0	0	0
Sugar olig.	0	0.018	0.018	0	0	0	0	0	0	0	0.018	0	0.018	0	0	0
Ethanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	0.424	0.381	0.403	0	0	0	0	0	0	0	0.696	0.227	0.469	0	0	0
Furfural	0.038	0	0.002	0	0	0	0	0	0	0	0.002	0.001	0.001	0	0	0
H_2SO_4	1.098	0.012	0.07	0	0	0	0	0	0	0	0.07	0	0.07	0	0	0
N_2	0	0	0	0	0	86.9	86.9	86.9	8.69	78.21	8.69	8.69	0	0	0	0
CO_2	0	0	0	0	0	0	0	0	0	0	0.529	0.529	0	0	0	0
O_2	0	0	0	0	0	23.1	23.1	23.1	2.31	20.79	1.937	1.937	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0.408	0	0	0	0	0	0	0.376	0.354	0.022	4.08	0	0
Acetic Acid	0.008	0.003	0.003	0	0	0	0	0	0	0	0.003	0.001	0.003	0	0	0
Glycerol	0	0.002	0.002	0	0	0	0	0	0	0	0.002	0	0.002	0	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CSL	0	0	0	0	0.007	0	0	0	0	0	0.007	0	0.007	0	0	23.612
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10.2	0
SO_2	0	0	0	0.408	0	0	0	0	0	0	0.406	0.4	0.006	4.08	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0.13	0.018	0.025	0	0	0	0	0	0	0	0.025	0	0.025	0	0	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0.001	0.001	0	0	0	0	0	0	0	0.001	0	0.001	0	0	0
Lignin	0	0.002	0.002	0	0	0	0	0	0	0	0.002	0	0.002	0	0	0
Cellulase	0	0.005	0.005	0	0	0	0	0	0	0	0.005	0	0.005	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0.188	0	0.188	0	0	0
ZYMO	0	0.005	0.005	0	0	0	0	0	0	0	0.005	0	0.005	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0.001	0.001	0	0	0	0	0	0	0	0	0	0	0	0	0
Others	5.103	0.059	0.328	0	0	0	0	0	0	0	0.328	0	0.328	0	0	0
Ash	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table A.26 : Aspen Plus simulation software mass flows for CS-2 (S99-S111).

Components	S99	S100	S101	S102	S103	S104	S105	S106	S107	S108	S109	S110	S111
Total flow	33.812	12.138	130.682	130.682	148.794	303.067	108.533	120.672	194.533	38.907	155.627	3880.078	3880.078
Glucose	0	0	0.283	0.283	0.898	0	0	0	0	0	0	28.79	28.79
Xylose	0	0	0.335	0.335	2.879	0	0	0	0	0	0	119.061	119.061
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0	0.164	0.164	0.226	0.23	0	0	0.23	0.046	0.184	2.895	2.895
Oth. sugar mono.	0	0	1.821	1.821	9.912	0	0	0	0	0	0	378.606	378.606
Sugar olig.	0	0	4.434	4.434	4.434	4.452	0	0	4.452	0.89	3.562	0	0
Ethanol	0	0	0	0	0	0	0	0	0	0	0	45.561	45.561
Water	0	0	94.884	94.884	95.308	102.904	1.839	2.066	101.065	20.213	80.852	392.157	392.157
Furfural	0	0	0.006	0.006	0.043	0.044	0.002	0.002	0.043	0.009	0.034	2.027	2.027
H_2SO_4	0	0	3.033	3.033	4.131	4.201	0	0	4.201	0.84	3.361	51.371	51.371
N_2	0	0	0	0	0	78.21	78.208	86.898	0.002	0	0.001	0	0
CO_2	0	0	0	0	0	13.22	13.207	13.736	0.013	0.003	0.011	0	0
O_2	0	0	0	0	0	11.373	11.373	13.31	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	3.372	1.048	1.402	2.324	0.465	1.859	0	0
Acetic Acid	0	0	0.743	0.743	0.751	0.753	0.009	0.01	0.744	0.149	0.595	0.49	0.49
Glycerol	0	0	0.526	0.526	0.526	0.528	0	0	0.528	0.106	0.422	0	0
DAP	0	0	0	0	0	0	0	0	0	0	0	0	0
CSL	23.612	0	0	0	0	23.619	0	0	23.619	4.724	18.895	0	0
Nutrients	10.2	0	0	0	0	10.2	0	0	10.2	2.04	8.16	0	0
SO_2	0	0	0	0	0	4.031	2.847	3.247	1.184	0.237	0.947	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0	0	4.244	4.244	4.374	4.398	0	0	4.398	0.879	3.517	6.077	6.077
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0.113	0.113	0.113	0	0	0	0	0	0	1889.747	1889.747
Xylan	0	0	0.196	0.196	0.196	0.197	0	0	0.197	0.039	0.158	157.616	157.616
Lignin	0	0	0.392	0.392	0.392	0.393	0	0	0.393	0.079	0.315	314.236	314.236
Cellulase	0	0	1.295	1.295	1.295	3.12	0	0	3.12	0.624	2.496	0	0
Biomass	0	0	0.056	0.056	0.056	2.239	0	0	2.239	0.448	1.791	0	0
ZYMO	0	0	1.353	1.353	1.353	1.358	0	0	1.358	0.272	1.087	0	0
Acetate	0	0	0.04	0.04	0.04	0.041	0	0	0.041	0.008	0.032	32.415	32.415
Oth. sugar poly.	0	0	0.23	0.23	0.23	0.072	0	0	0.072	0.014	0.058	184.802	184.802
Others	0	12.138	14.829	14.829	19.932	32.398	0	0	32.398	6.48	25.919	238.779	238.779
Ash	0	0	0.044	0.044	0.044	0.044	0	0	0.044	0.009	0.035	35.415	35.415

Table A.27 : Aspen Plus simulation software mass flows for CS-2 (S112-S124).

Components	S112	S113	S114	S115	S116	S117	S118	S119	S120	S121	S122	S123	S124
Total flow	453.539	4489.244	4489.244	16.719	1.103	4040.32	448.924	1.92	0.218	451.062	451.062	118.006	333.056
Glucose	0	1919.666	1919.666	0	0	1727.699	191.967	0	0	191.967	6.335	0	6.335
Xylose	0	119.061	119.061	0	0	107.155	11.906	0	0	11.906	1.024	0	1.024
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	3.079	3.079	0	0	2.771	0.308	0	0	0.308	0.308	0	0.308
Oth. sugar mono.	0	378.606	378.606	0	0	340.746	37.861	0	0	37.861	4.771	0	4.771
Sugar olig.	0	79.152	79.152	0	0	71.237	7.915	0	0	7.915	7.915	0	7.915
Ethanol	0	45.561	45.561	0	0	41.005	4.556	0	0	4.556	113.278	11.975	101.303
Water	414.434	697.157	697.157	0	0	627.441	69.716	0	0	69.716	71.787	2.912	68.875
Furfural	0	2.061	2.061	0	0	1.855	0.206	0	0	0.206	0.206	0.004	0.203
H_2SO_4	0	54.732	54.732	0	0	49.259	5.473	0	0	5.473	5.473	0	5.473
N_2	0	0.001	0.001	0	0	0.001	0	0	0	0	0	0	0
CO_2	0	0.011	0.011	0	0	0.01	0.001	0	0	0.001	102.97	102.361	0.61
O_2	0	0	0	0	0	0	0	0	0	0	0.546	0.546	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	1.859	1.859	0	0	1.673	0.186	0	0	0.186	0.186	0.097	0.089
Acetic Acid	0	1.085	1.085	0	0	0.976	0.108	0	0	0.108	3.685	0.05	3.635
Glycerol	0	0.422	0.422	0	0	0.38	0.042	0	0	0.042	0.98	0	0.98
DAP	0	0	0	0	1.103	0	0	0	0.218	0.218	0.09	0	0.09
CSL	0	18.895	18.895	16.719	0	17.006	1.89	1.92	0	3.809	3.355	0	3.355
Nutrients	0	8.16	8.16	0	0	7.344	0.816	0	0	0.816	0.816	0	0.816
SO_2	0	0.947	0.947	0	0	0.852	0.095	0	0	0.095	0.095	0.062	0.033
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0	9.594	9.594	0	0	8.635	0.96	0	0	0.96	3.838	0	3.838
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	90.708	90.708	0	0	81.637	9.071	0	0	9.071	9.071	0	9.071
Xylan	0	157.774	157.774	0	0	141.996	15.777	0	0	15.777	15.777	0	15.777
Lignin	0	314.551	314.551	0	0	283.095	31.455	0	0	31.455	31.455	0	31.455
Cellulase	39.105	41.601	41.601	0	0	37.441	4.16	0	0	4.16	4.16	0	4.16
Biomass	0	1.791	1.791	0	0	1.612	0.179	0	0	0.179	0.179	0	0.179
ZYMO	0	1.087	1.087	0	0	0.978	0.109	0	0	0.109	8.039	0	8.039
Acetate	0	32.447	32.447	0	0	29.202	3.245	0	0	3.245	3.245	0	3.245
Oth. sugar poly.	0	184.859	184.859	0	0	166.373	18.486	0	0	18.486	18.486	0	18.486
Others	0	264.697	264.697	0	0	238.228	26.47	0	0	26.47	26.47	0	26.47
Ash	0	35.45	35.45	0	0	31.905	3.545	0	0	3.545	3.545	0	3.545

Table A.28 : Aspen Plus simulation software mass flows for CS-2 (S125-S136).

Components	S125	S126	S127	S128	S129	S130	S131	S132	S133	S134	S135	S136
Total flow	4391.198	131.736	4259.462	131.736	4259.462	3294.771	1405.892	4700.663	1096.428	4700.663	4700.663	8
Glucose	1734.034	52.021	1682.013	0	5.046	5.046	0	5.046	0	5.046	5.046	0
Xylose	108.178	3.245	104.933	0	5.981	5.981	0	5.981	0	5.981	5.981	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	3.079	0.092	2.987	0.092	2.987	3.079	0	3.079	0	3.079	3.079	0
Oth. sugar mono.	345.516	10.365	335.15	0	32.51	32.51	0	32.51	0	32.51	32.51	0
Sugar olig.	79.152	2.375	76.777	2.375	76.777	79.152	0	79.152	0	79.152	79.152	0
Ethanol	142.308	4.269	138.039	4.269	1146.571	1038.156	118.403	1156.559	112.684	1156.559	1156.559	1.091
Water	696.316	20.889	675.427	20.889	683.318	677.231	1284.782	1962.013	26.977	1962.013	1962.013	0.215
Furfural	2.058	0.062	1.996	0.062	1.996	2.026	0.036	2.061	0.032	2.061	2.061	0
H_2SO_4	54.732	1.642	53.09	1.642	53.09	54.732	0	54.732	0	54.732	54.732	0
N_2	0.001	0	0.001	0	0.001	0	0	0	0.001	0	0	0
CO_2	0.619	0.019	0.601	0.019	956.204	6.215	1.079	7.295	950.007	7.295	7.295	6.634
O_2	0.001	0	0.001	0	4.798	0.002	0	0.003	4.795	0.003	0.003	0.003
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	1.762	0.053	1.709	0.053	1.709	0.859	0.884	1.743	0.903	1.743	1.743	0.036
Acetic Acid	4.611	0.138	4.472	0.138	35.864	35.542	0.511	36.053	0.461	36.053	36.053	0
Glycerol	1.36	0.041	1.319	0.041	9.548	9.588	0	9.588	0	9.588	9.588	0
DAP	1.194	0.036	1.158	0.036	0.604	0.64	0	0.64	0	0.64	0.64	0
CSL	37.08	1.112	35.968	1.112	33.995	35.108	0	35.108	0	35.108	35.108	0
Nutrients	8.16	0.245	7.915	0.245	7.915	8.16	0	8.16	0	8.16	8.16	0
SO_2	0.885	0.027	0.859	0.027	0.859	0.319	0.196	0.515	0.566	0.515	0.515	0.021
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	12.472	0.374	12.099	66.006	37.402	103.407	0.002	103.407	0.001	103.407	103.407	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	90.708	2.721	87.987	2.721	87.987	90.708	0	90.708	0	90.708	90.708	0
Xylan	157.774	4.733	153.04	4.733	153.04	157.774	0	157.774	0	157.774	157.774	0
Lignin	314.551	9.437	305.114	9.437	305.114	314.551	0	314.551	0	314.551	314.551	0
Cellulase	41.601	1.248	40.353	1.248	40.353	41.601	0	41.601	0	41.601	41.601	0
Biomass	1.791	0.054	1.738	0.054	1.738	1.791	0	1.791	0	1.791	1.791	0
ZYMO	9.017	0.271	8.747	0.271	43.195	43.465	0	43.465	0	43.465	43.465	0
Acetate	32.447	0.973	31.474	0.973	31.474	32.447	0	32.447	0	32.447	32.447	0
Oth. sugar poly.	184.859	5.546	179.314	5.546	179.314	184.859	0	184.859	0	184.859	184.859	0
Others	264.697	7.941	256.757	7.941	256.757	264.697	0	264.697	0	264.697	264.697	0
Ash	35.45	1.063	34.386	1.063	34.386	35.45	0	35.45	0	35.45	35.45	0

Table A.29 : Aspen Plus simulation software mass flows for CS-2 (S137-S148).

Components	S137	S138	S139	S140	S141	S142	S143	S144	S145	S146	S147	S148
Total flow	1581	3111.663	1222.434	1294.5	1111.042	1350	231	1350	1154.872	195.128	1154.872	195.128
Glucose	0	5.046	0	0	0	0	0	0	0	0	0	0
Xylose	0	5.981	0	0	0	0	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0.001	3.078	0	0	0	0	0.001	0	0	0	0	0
Oth. sugar mono.	0	32.51	0	0	0	0	0	0	0	0	0	0
Sugar olig.	0	79.152	0	0	0	0	0	0	0	0	0	0
Ethanol	1155.465	0.003	125.75	0	7.347	1155.465	0	1155.465	1153.154	2.311	1153.154	2.311
Water	419.041	1542.758	30.104	1294.5	39.822	190.848	228.192	190.848	1.718	189.131	1.718	189.131
Furfural	0.825	1.237	0.036	0	0	0.825	0	0.825	0	0.825	0	0.825
H_2SO_4	0.001	54.731	0	0	0	0	0.001	0	0	0	0	0
N_2	0	0	0.001	0	0.001	0	0	0	0	0	0	0
CO_2	0.661	0	1059.002	0	1057.923	0.661	0	0.661	0	0.661	0	0.661
O_2	0	0	5.343	0	5.343	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	1.707	0	1.036	0	0.152	1.707	0	1.707	0	1.707	0	1.707
Acetic Acid	2.756	33.296	0.511	0	0	0	2.756	0	0	0	0	0
Glycerol	0	9.588	0	0	0	0	0	0	0	0	0	0
DAP	0	0.64	0	0	0	0	0	0	0	0	0	0
CSL	0	35.108	0	0	0	0	0	0	0	0	0	0
Nutrients	0	8.16	0	0	0	0	0	0	0	0	0	0
SO_2	0.494	0	0.649	0	0.454	0.494	0	0.494	0	0.494	0	0.494
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0.049	103.358	0.002	0	0	0	0.049	0	0	0	0	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	90.708	0	0	0	0	0	0	0	0	0	0
Xylan	0	157.774	0	0	0	0	0	0	0	0	0	0
Lignin	0	314.551	0	0	0	0	0	0	0	0	0	0
Cellulase	0	41.601	0	0	0	0	0	0	0	0	0	0
Biomass	0	1.791	0	0	0	0	0	0	0	0	0	0
ZYMO	0	43.465	0	0	0	0	0	0	0	0	0	0
Acetate	0	32.447	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	184.859	0	0	0	0	0	0	0	0	0	0
Others	0	264.697	0	0	0	0	0	0	0	0	0	0
Ash	0	35.45	0	0	0	0	0	0	0	0	0	0

Table A.30 : Aspen Plus simulation software mass flows for CS-2 (S149-S160).

Components	S149	S150	S151	S152	S153	S154	S155	S156	S157	S158	S159	S160
Total flow	3111.663	1573.536	1573.536	1538.127	1538.127	587.303	950.824	146.826	147	440.477	1649.999	30.915
Glucose	5.046	0	0	5.046	5.046	4.541	0.505	1.135	0	3.406	0	0
Xylose	5.981	0	0	5.981	5.981	5.383	0.598	1.346	0	4.037	0.002	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	3.078	0.154	0.154	2.925	2.925	2.632	0.292	0.658	0	1.974	1.454	0
Oth. sugar mono.	32.51	0	0	32.51	32.51	29.259	3.251	7.315	0	21.944	0.005	0
Sugar olig.	79.152	0	0	79.152	79.152	71.237	7.915	17.809	0	53.427	0	0
Ethanol	0.003	0.003	0.003	0	0	0	0	0	0	0	0.003	0
Water	1542.758	1516.672	1516.672	26.086	26.086	23.477	2.609	5.869	147	17.608	1534.266	0
Furfural	1.237	1.138	1.138	0.099	0.099	0.089	0.01	0.022	0	0.067	1.203	0
H_2SO_4	54.731	0.595	0.595	54.137	54.137	48.723	5.414	12.181	0	36.542	19.014	0
N_2	0	0	0	0	0	0	0	0	0	0	0	24.423
CO_2	0	0	0	0	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	6.492
CH_4	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	33.296	32.292	32.292	1.004	1.004	0.904	0.1	0.226	0	0.678	32.968	0
Glycerol	9.588	0.205	0.205	9.384	9.384	8.445	0.938	2.111	0	6.334	2.93	0
DAP	0.64	0	0	0.64	0.64	0	0.64	0	0	0	0	0
CSL	35.108	0	0	35.108	35.108	0	35.108	0	0	0	0	0
Nutrients	8.16	0	0	8.16	8.16	0	8.16	0	0	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	103.358	22.47	22.47	80.888	80.888	67.973	12.915	16.993	0	50.98	57.609	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	90.708	0	0	90.708	90.708	1.814	88.894	0.454	0	1.361	0	0
Xylan	157.774	0	0	157.774	157.774	3.155	154.618	0.789	0	2.367	0	0
Lignin	314.551	0	0	314.551	314.551	6.291	308.26	1.573	0	4.718	0	0
Cellulase	41.601	0	0	41.601	41.601	20.801	20.801	5.2	0	15.601	0	0
Biomass	1.791	0	0	1.791	1.791	0.896	0.896	0.224	0	0.672	0	0
ZYMO	43.465	0	0	43.465	43.465	21.733	21.733	5.433	0	16.299	0	0
Acetate	32.447	0	0	32.447	32.447	0.649	31.798	0.162	0	0.487	0	0
Oth. sugar poly.	184.859	0	0	184.859	184.859	3.697	181.162	0.924	0	2.773	0	0
Others	264.697	0.008	0.008	264.688	264.688	238.22	26.469	59.555	0	178.664	0.546	0
Ash	35.45	0	0	35.45	35.45	0.709	34.741	0.177	0	0.532	0	0

Table A.31 : Aspen Plus simulation software mass flows for CS-2 (S161-S174).

Components	S161	S162	S163	S164	S165	S166	S167	S168	S169	S170	S171	S173	S174
Total flow	30.915	30.915	31.175	950.564	1142.217	48.978	391.5	48.978	27.485	364.014	1314.579	27.485	524.826
Glucose	0	0	0	0.505	0	0	3.406	0	0	3.406	3.911	0	1.135
Xylose	0	0	0	0.598	0	0	4.037	0	0.002	4.035	4.634	0.002	1.346
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0	0	0.292	0	0.632	1.342	0.632	0.667	0.674	0.967	0.667	0.659
Oth. sugar mono.	0	0	0	3.251	0	0	21.944	0	0.004	21.94	25.191	0.004	7.315
Sugar olig.	0	0	0	7.915	0	0	53.427	0	0	53.427	61.343	0	17.809
Ethanol	0	0	0	0	7.347	0	0	0	0	0	0	0	0
Water	0	0	0.254	2.355	40.075	17.126	0.482	17.126	0.468	0.014	2.369	0.468	381.062
Furfural	0	0	0	0.01	0	0.058	0.009	0.058	0.008	0.001	0.011	0.008	0.022
H_2SO_4	0	0	0	5.414	0	5.813	30.73	5.813	12.607	18.123	23.536	12.607	12.182
N_2	24.423	24.423	24.422	0.001	24.423	0	0	0	0	0	0.001	0	0
CO_2	0	0	0	0	1057.923	0	0	0	0	0	0	0	0
O_2	6.492	6.492	6.492	0	11.835	0	0	0	0	0	0	0	0
CH_4	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	0	0	0	0.152	0	0	0	0	0	0	0	0
Acetic Acid	0	0	0.006	0.094	0.006	0.642	0.035	0.642	0.033	0.002	0.096	0.033	2.982
Glycerol	0	0	0	0.938	0	1.087	5.247	1.087	1.639	3.609	4.547	1.639	2.112
DAP	0	0	0	0.64	0	0	0	0	0	0	0.64	0	0
CSL	0	0	0	35.108	0	0	0	0	0	0	35.108	0	0
Nutrients	0	0	0	8.16	0	0	0	0	0	0	8.16	0	0
SO_2	0	0	0	0	0.454	0	0	0	0	0	0	0	0
H_2S	0	0	0	0	0	0	0	0	0	0	0	0	0
Oth. inorg.acids	0	0	0.001	12.913	0.001	23.484	27.496	23.484	11.655	15.841	28.754	11.655	17.042
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	88.894	0	0	1.361	0	0	1.361	90.254	0	0.454
Xylan	0	0	0	154.618	0	0	2.367	0	0	2.367	156.985	0	0.789
Lignin	0	0	0	308.26	0	0	4.718	0	0	4.718	312.978	0	1.573
Cellulase	0	0	0	20.801	0	0	15.601	0	0	15.601	36.401	0	5.2
Biomass	0	0	0	0.896	0	0	0.672	0	0	0.672	1.567	0	0.224
ZYMO	0	0	0	21.733	0	0	16.299	0	0	16.299	38.032	0	5.433
Acetate	0	0	0	31.798	0	0	0.487	0	0	0.487	32.285	0	0.162
Oth. sugar poly.	0	0	0	181.162	0	0	2.773	0	0	2.773	183.935	0	0.924
Others	0	0	0	26.469	0	0.135	178.529	0.135	0.402	178.127	204.596	0.402	59.555
Ash	0	0	0	34.741	0	0	0.532	0	0	0.532	35.273	0	0.177

Table A.32 : Aspen Plus simulation software mass flows for CS-2 (S175-S186).

Components	S175	S176	S177	S178	S179	S180	S181	S182	S183	S184	S185	S186
Total flow	393.619	2238.746	1152.31	17842.91	17842.91	7.522	17850.43	17850.43	191.282	17659.15	0.033	6733.64
Glucose	0.852	0.852	0.039	0.891	0.891	0	0.891	0.062	0	0.062	0	0
Xylose	1.009	1.011	0.046	1.058	1.058	0	1.058	0.074	0	0.074	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0.494	1.948	0.01	4.904	4.904	0	4.904	0.343	0	0.343	0	0
Oth. sugar mono.	5.485	5.49	0.252	5.742	5.742	0	5.742	0.402	0	0.402	0	0
Sugar olig.	13.357	13.357	0.613	13.97	13.97	0	13.97	0.978	0	0.978	0	0
Ethanol	0	2.313	0	2.313	2.313	0	2.313	0.162	0.001	0.161	0	0
Water	285.796	2009.193	1147.717	17579.56	17579.56	0	17579.56	17578.59	6.144	17572.44	0	0
Furfural	0.017	2.045	0	2.046	2.046	0	2.046	0.143	0.001	0.143	0	0
H_2SO_4	9.136	28.151	0.004	39.377	39.377	0	39.377	39.377	0	39.377	0	0
N_2	0	0	0	0	0	0	0	0	0	0	0	5319.576
CO_2	0	0.661	0	0.661	0.661	0	0.661	155.827	144.856	10.971	0	0
O_2	0	0	0	0	0	0	0	0	0	0	0	1414.064
CH_4	0	0	0	0	0	0	0	40.351	40.214	0.138	0	0
NO_x	0	0	0	0	0	0	0	0	0	0	0	0
NH_3	0	1.707	0	1.707	1.707	0	1.707	5.552	0.039	5.512	0	0
Acetic Acid	2.237	35.204	0	46.737	46.737	0	46.737	3.272	0.001	3.271	0	0
Glycerol	1.584	4.514	0.045	4.559	4.559	0	4.559	0.319	0	0.319	0	0
DAP	0	0	0.641	0.641	0.641	0	0.641	0.641	0	0.641	0	0
CSL	0	0	0.351	0.351	0.351	0	0.351	0.351	0	0.351	0	0
Nutrients	0	0	0	0	0	7.522	7.522	7.522	0	7.522	0.033	0
SO_2	0	0.494	0	0.494	0.494	0	0.494	0.494	0.016	0.477	0	0
H_2S	0	0	0	0	0	0	0	0.076	0.01	0.065	0	0
Oth. inorg.acids	12.782	70.392	0.279	74.174	74.174	0	74.174	5.193	0	5.193	0	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0.34	0.34	0	0.34	0.34	0	0.34	0.024	0	0.024	0	0
Xylan	0.592	0.592	0	0.592	0.592	0	0.592	0.041	0	0.041	0	0
Lignin	1.18	1.18	0	1.18	1.18	0	1.18	0.083	0	0.083	0	0
Cellulase	3.9	3.9	0	3.9	3.9	0	3.9	0.273	0	0.273	0	0
Biomass	0.168	0.168	0	0.168	0.168	0	0.168	6.1	0	6.1	0	0
ZYMO	4.075	4.075	0	4.075	4.075	0	4.075	0.285	0	0.285	0	0
Acetate	0.122	0.122	0	0.122	0.122	0	0.122	0.009	0	0.009	0	0
Oth. sugar poly.	0.693	0.693	0	0.693	0.693	0	0.693	0.048	0	0.048	0	0
Others	44.666	45.212	2.046	47.259	47.259	0	47.259	3.308	0	3.308	0	0
Ash	0.133	0.133	0	0.133	0.133	0	0.133	0.133	0	0.133	0	0

Table A.33 : Aspen Plus simulation software mass flows for CS-2 (S187-S200).

Components	S187	S188	S189	S190	S191	S192	S193	S194	S195	S196	S197	S198	S199	S200
Total flow	24401.09	6856.481	7047.76	17544.6	254.25	17290.35	127.525	126.73	63.64	63.87	8.274	55.37	22.87	32.50
Glucose	0.006	0	0	0.006	0	0.006	0	0	0	0	0	0	0	0
Xylose	0.007	0	0	0.007	0	0.007	0	0	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0.034	0	0	0.034	0	0.034	0	0	0	0	0	0	0	0
Oth. sugar mono.	0.04	0	0	0.04	0	0.04	0	0	0	0	0	0	0	0
Sugar olig.	0.098	0	0	0.098	0.001	0.096	0.001	0.001	0	0	0	0	0	0
Ethanol	0.016	0.002	0.003	0.014	0	0.014	0	0	0	0	0	0	0	0
Water	17583.42	106.938	113.081	17476.4	240.945	17235.53	114.613	126.32	50.93	63.67	6.622	44.31	22.85	21.4
Furfural	0.014	0.001	0.002	0.013	0	0.013	0	0	0	0	0	0	0	0
H_2SO_4	39.392	0	0	39.392	0.543	38.849	0.258	0.285	0.115	0.144	0.015	0.1	0	0.1
N_2	5319.625	5319.357	5319.35	0.268	0.004	0.265	0.002	0.002	0.001	0.001	0	0.001	0.001	0
CO_2	23.071	23.008	167.865	0.063	0.001	0.062	0	0	0	0	0	0	0	0
O_2	1406.371	1406.232	1406.23	0.139	0.002	0.137	0.001	0.001	0	0.001	0	0	0	0
CH_4	0.138	0.138	40.351	0	0	0	0	0	0	0	0	0	0	0
NO_x	0.324	0.064	0.064	0.259	0.004	0.256	0.002	0.002	0.001	0.001	0	0.001	0.001	0
NH_3	5.514	0.465	0.504	5.049	0.07	4.98	0.033	0.037	0.015	0.018	0.002	0.013	0.012	0.001
Acetic Acid	0.327	0.001	0.002	0.326	0.004	0.321	0.002	0.002	0.001	0.001	0	0.001	0	0.001
Glycerol	0.032	0	0	0.032	0	0.031	0	0	0	0	0	0	0	0
DAP	0.641	0	0	0.641	0.009	0.633	0.004	0.005	0.002	0.002	0	0.002	0	0.002
CSL	0.351	0	0	0.351	0.005	0.346	0.002	0.003	0.001	0.001	0	0.001	0	0.001
Nutrients	7.558	0	0	7.558	0.104	7.454	0.05	0.055	0.022	0.028	0.003	0.019	0	0.019
SO_2	0.484	0.223	0.24	0.261	0.004	0.257	0.002	0.002	0.001	0.001	0	0.001	0.001	0
H_2S	0.066	0.054	0.064	0.012	0	0.012	0	0	0	0	0	0	0	0
Oth. inorg.acids	0.518	0	0	0.518	0.007	0.512	0.003	0.003	0.001	0.002	0	0.001	0	0.001
Undecane	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0.002	0	0	0.002	0.002	0	0.002	0	0.002	0	0	0.002	0	0.002
Xylan	0.004	0	0	0.004	0.004	0	0.004	0	0.004	0	0.001	0.004	0	0.004
Lignin	0.008	0	0	0.008	0.008	0	0.008	0	0.008	0	0.001	0.007	0	0.007
Cellulase	0.028	0	0	0.028	0.028	0	0.028	0	0.028	0	0.004	0.024	0	0.024
Biomass	12.317	0	0	12.317	12.317	0	12.317	0	12.31	0	1.601	10.71	0	10.71
ZYMO	0.029	0	0	0.029	0.029	0	0.029	0	0.029	0	0.004	0.025	0	0.025
Acetate	0.001	0	0	0.001	0.001	0	0.001	0	0.001	0	0	0.001	0	0.001
Oth. sugar poly.	0.005	0	0	0.005	0.005	0	0.005	0	0.005	0	0	0.004	0	0.004
Others	0.428	0	0	0.428	0.006	0.423	0.003	0.003	0.001	0.001	0	0.001	0	0.001
Ash	0.153	0	0	0.153	0.153	0	0.153	0	0.153	0	0.02	0.133	0	0.133

Table A.34 : Aspen Plus simulation software mass flows for CS-2 (S201-S212).

Components	S201	S202	S203	S204	S205	S206	S207	S208	S209	S210	S211	S212
Total flow	22.872	17503.84	8492.249	17147.37	695.809	4427.634	695.809	5123.443	22223.63	47.18	22223.63	8655.119
Glucose	0	0.006	3.911	0.039	0	0	0	0	0.039	0	0.039	0
Xylose	0	0.007	4.634	0.046	0	0	0	0	0.046	0	0.046	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0.034	0.967	0.01	0	0	0	0	0.01	0	0.01	0
Oth. sugar mono.	0	0.04	25.191	0.252	0	0	0	0	0.252	0	0.252	0
Sugar olig.	0	0.098	61.343	0.613	0	0	0	0	0.613	0	0.613	0
Ethanol	0	0.014	0.003	0	0	0	0	0	0	0	0	0
Water	22.857	17448.4	147.242	975.052	178.066	0	178.066	178.066	1153.118	0	1153.118	0
Furfural	0	0.013	0.013	0	0	0	0	0	0	0	0	0
H_2SO_4	0	39.277	23.636	0.004	0	0	0	0	0.004	0	0.004	0
N_2	0.001	0.268	5319.357	12179.47	0	3396.363	0	3396.363	15575.83	0	15575.83	6837.544
CO_2	0	0.063	167.865	2599.056	0	0	0	891.668	3490.724	0	3490.724	0
O_2	0	0.139	1406.232	1325.904	265.388	1031.271	265.388	648.342	1974.247	0	1974.247	1817.575
CH_4	0	0	40.351	0.404	0	0	0	0	0.404	0	0.404	0
NO_x	0.001	0.259	0.064	1	5.869	0	5.869	5.869	6.869	0	6.869	0
NH_3	0.012	5.047	0.505	0	0	0	0	0	0	0	0	0
Acetic Acid	0	0.325	16.831	0.168	0	0	0	0	0.168	0	0.168	0
Glycerol	0	0.032	4.547	0.045	0	0	0	0	0.045	0	0.045	0
DAP	0	0.64	0.641	0.641	0	0	0	0	0.641	0	0.641	0
CSL	0	0.35	35.108	0.351	0	0	0	0	0.351	0	0.351	0
Nutrients	0	7.536	8.179	0	0	0	0	0	0	0	0	0
SO_2	0.001	0.261	0.24	16.976	0	0	0	0	16.976	0	16.976	0
H_2S	0	0.012	0.064	0	0.677	0	0.677	0.677	0.677	0	0.677	0
Oth. inorg.acids	0	0.517	30.733	0.308	0	0	0	0	0.308	0	0.308	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	90.256	0.903	0	0	0	0	0	0.903	0	0
Xylan	0	0	156.988	1.57	0	0	0	0	0	1.57	0	0
Lignin	0	0	312.985	3.13	0	0	0	0	0	3.13	0	0
Cellulase	0	0	36.425	0.364	0	0	0	0	0	0.364	0	0
Biomass	0	0	12.283	0.123	0	0	0	0	0	0.123	0	0
ZYMO	0	0	38.057	0.381	0	0	0	0	0	0.381	0	0
Acetate	0	0	32.286	0.323	0	0	0	0	0	0.323	0	0
Oth. sugar poly.	0	0	183.939	1.84	0	0	0	0	0	1.84	0	0
Others	0	0.428	272.959	2.73	245.809	0	245.809	2.458	2.046	3.142	2.046	0
Ash	0	0	35.406	35.406	0	0	0	0	0	35.406	0	0

Table A.35 : Aspen Plus simulation software mass flows for CS-2 (S213-S224).

Components	S213	S214	S215	S216	S217	S218	S219	S220	S221	S222	S223	S224
Total flow	8655.119	22223.63	21075.93	1147.708	21071.32	4.602	13688.83	13688.83	13688.83	13688.83	13688.83	13688.83
Glucose	0	0.039	0.039	0	0	0.039	0	0	0	0	0	0
Xylose	0	0.046	0.046	0	0	0.046	0	0	0	0	0	0
Soluble lignin	0	0	0	0	0	0	0	0	0	0	0	0
HMF	0	0.01	0.01	0	0	0.01	0	0	0	0	0	0
Oth. sugar mono.	0	0.252	0.252	0	0	0.252	0	0	0	0	0	0
Sugar olig.	0	0.613	0.613	0	0	0.613	0	0	0	0	0	0
Ethanol	0	0	0	0	0	0	0	0	0	0	0	0
Water	0	1153.118	5.41	1147.708	5.401	0.01	13688.83	13688.83	13688.83	13688.83	13688.83	13688.83
Furfural	0	0	0	0	0	0	0	0	0	0	0	0
H_2SO_4	0	0.004	0.004	0	0	0.004	0	0	0	0	0	0
N_2	6837.544	15575.83	15575.83	0	15575.83	0	0	0	0	0	0	0
CO_2	0	3490.72	3490.72	0	3490.724	0	0	0	0	0	0	0
O_2	1817.575	1974.24	1974.24	0	1974.247	0	0	0	0	0	0	0
CH_4	0	0.404	0.404	0	0.404	0	0	0	0	0	0	0
NO_x	0	6.869	6.869	0	6.869	0	0	0	0	0	0	0
NH_3	0	0	0	0	0	0	0	0	0	0	0	0
Acetic Acid	0	0.168	0.168	0	0.168	0	0	0	0	0	0	0
Glycerol	0	0.045	0.045	0	0	0.045	0	0	0	0	0	0
DAP	0	0.641	0.641	0	0	0.641	0	0	0	0	0	0
CSL	0	0.351	0.351	0	0	0.351	0	0	0	0	0	0
Nutrients	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	16.976	16.976	0	16.975	0	0	0	0	0	0	0
H_2S	0	0.677	0.677	0	0.677	0	0	0	0	0	0	0
Oth. inorg.acids	0	0.308	0.308	0	0.029	0.279	0	0	0	0	0	0
Undecane	0	0	0	0	0	0	0	0	0	0	0	0
Cellulose	0	0	0	0	0	0	0	0	0	0	0	0
Xylan	0	0	0	0	0	0	0	0	0	0	0	0
Lignin	0	0	0	0	0	0	0	0	0	0	0	0
Cellulase	0	0	0	0	0	0	0	0	0	0	0	0
Biomass	0	0	0	0	0	0	0	0	0	0	0	0
ZYMO	0	0	0	0	0	0	0	0	0	0	0	0
Acetate	0	0	0	0	0	0	0	0	0	0	0	0
Oth. sugar poly.	0	0	0	0	0	0	0	0	0	0	0	0
Others	0	2.046	2.046	0	0	2.046	0	0	0	0	0	0
Ash	0	0	0	0	0	0	0	0	0	0	0	0

APPENDIX B

This section provides tables that include stream temperature and pressure for CS-1 and CS-2. While Table B.1 and Table B.2 present the results of CS-1, Table B.3 and Table B.4 show the results of CS-2.

Table B.1 : Aspen Plus simulation software stream temperatures and pressures for CS-1 (S1-S123).

Stream No	Tem. (^{0}C)	Pres. (atm)	Stream No	Tem. (^{0}C)	Pres. (atm)	Stream No	Tem. (^{0}C)	Pres. (atm)
S1	19.1	1	S42	93.5	0.99	S83	130	0.4
S2	25	1	S43	100	0.99	S84	84.2	1
S3	25	1	S44	93.8	1	S85	99.4	1
S4	19.5	1	S45	84.2	1	S86	28	1
S5	20.2	19.74	S46	200	1	S87	20	1
S6	187.5	19.74	S47	25	1	S88	25	1
S7	190	19.74	S48	200	1	S89	176.3	3
S8	190	19.74	S49	200	1	S90	40	1
S9			S50	50	1	S91	40	1
S10	135	19.74	S51	130	0.4	S92	40	1
S11	135	19.74	S52	130	0.4	S93	28	1
S12			S53	59.5	0.2	S94	28	1
S13	135	19.74	S54	97	1.2	S95	28	1
S14	77	0.7	S55	96	1	S96	28	1
S15	60	1	S56	20	1	S97	15	1
S16	72.1	1	S57	25	1	S98	20	1
S17	60	1	S58	25	1	S99	19.3	1
S18	77	0.7	S59	100	1	S100	20	1
S19	25	1	S60	60.4	0.2	S101	84.2	1
S20	85.4	1	S61	60.4	0.2	S102	40	1
S21	67.2	1	S62	73	1	S103	43.6	1
S22	60	1	S63	60.4	0.2	S104	28	1.66
S23	25	1	S64	60.4	0.2	S105	25.2	1
S24	35	1	S65	91	1.5	S106	25.5	1
S25	35.3	1	S66	91	1.5	S107	25.2	1
S26	35.3	1	S67	91	1.5	S108	25.2	1
S27	35.3	1	S68	85	1	S109	25.2	1
S28	25	1	S69	60.4	0.2	S110	75.7	0.4
S29	27.2	1	S70	91	1.5	S111	67	1
S30	25	1	S71	91	1.5	S112	25	1
S31	25	1	S72	91	1.5	S113	65	1
S32	25	1	S73	84	1	S114	41	1
S33	249.1	1	S74	100	1	S115	20	1
S34	249.1	1	S75	37	1	S116	20	1
S35	34.8	1	S76	37	1	S117	41	1
S36	42.6	1	S77	37	1	S118	41	1
S37	90	1.1	S78	118.1	1	S119	20	1
S38	90	1.1	S79	60	1	S120	20	1
S39	90	1.1	S80	130	0.4	S121	40.8	1
S40	53.1	0.18	S81	130	0.4	S122	41	1
S41	58.1	0.18	S82	130	0.4	S123	41	1

Table B.2 : Aspen Plus simulation software stream temperatures and pressures for CS-1 (S124-S224).

Stream No	Tem. (^{0}C)	Pres. (atm)	Stream No	Tem. (^{0}C)	Pres. (atm)	Stream No	Tem. (^{0}C)	Pres. (atm)
S124	41	1	S165	36.9	0.7	S207	866.5	1
S125	40.7	1	S166	225.5	0.29	S208	950	1
S126	40.7	1	S167	225.5	0.29	S209	950	1
S127	40.7	1	S168	225.5	18.99	S210		
S128	41	1	S169	286	0.21	S211	220	1
S129	41	1	S170	286	0.21	S212	25	1
S130	41.1	1	S171	108.2	0.21	S213	27.8	1
S131	40.8	0.7	S173	286	8.3	S214	219	1
S132	39.2	0.7	S174	84.2	1	S215	25	1
S133	41.1	1	S175	84.2	1	S216	25	1
S134	78.7	1	S176	99.8	1	S217	25	1
S135	80.8	3	S177	23	1	S218	25	1
S136	55.2	1.86	S178	60.5	0.2	S219	107	1.28
S137	102.4	1.91	S179	35	0.2	S220	108.2	42.33
S138	118.1	2.1	S180	20	1	S221	108.2	42.33
S139	41.2	1	S181	35	0.2	S222	395.5	42.33
S140	25	1	S182	35	1	S223	395.5	42.33
S141	35.9	0.7	S183	35	1	S224	125.4	2.32
S142	93.2	1.7	S184	35	1			
S143	120.7	2	S185	20	1			
S144	114.8	1.7	S186	25	1			
S145	114.8	1.7	S187	21.1	1			
S146	114.8	1.7	S188	21.1	1			
S147	38	1	S189	21.6	1			
S148	35	1	S190	21.1	1			
S149	117	2	S191	21.1	1			
S150	117	0.38	S192	21.1	1			
S151	117	1.77	S193	21.1	1			
S152	117	0.38	S194	21.1	1			
S153	70	0.38	S195	21.1	1			
S154	70	3.2	S196	21.1	1			
S155	70	3.2	S197	21.1	1			
S156	70	3.2	S198	21.1	1			
S157	25	1	S199	100	1			
S158	70	3.2	S200	100	1			
S159	120.9	2	S201	25	1			
S160	25	1	S202	21.1	1			
S161	388.3	9.51	S203	32.8	0.21			
S162	40	9.51	S204	950	0.99			
S163	68.9	3.2	S205	25	1			
S164	68.9	3.2	S206	25	1			

Table B.3 : Aspen Plus simulation software stream temperatures and pressures for CS-2 (S1-S123).

Stream No	Tem. (^{0}C)	Pres. (atm)	Stream No	Tem. (^{0}C)	Pres. (atm)	Stream No	Tem. (^{0}C)	Pres. (atm)
S1	19.1	1	S42	93.5	0.99	S83	130	0.4
S2	25	1	S43	100	0.99	S84	84.2	1
S3	25	1	S44	93.8	1	S85	100.1	1
S4	19.5	1	S45	84.2	1	S86	28	1
S5	20.2	19.74	S46	200	1	S87	20	1
S6	187.5	19.74	S47	25	1	S88	25	1
S7	190	19.74	S48	200	1	S89	176.3	3
S8	190	19.74	S49	200	1	S90	40	1
S9			S50	50	1	S91	40	1
S10	135	19.74	S51	130	0.4	S92	40	1
S11	135	19.74	S52	130	0.4	S93	28	1
S12			S53	59.5	0.2	S94	28	1
S13	135	19.74	S54	97	1.2	S95	28	1
S14	77	0.7	S55	96	1	S96	28	1
S15	60	1	S56	20	1	S97	15	1
S16	71.8	1	S57	25	1	S98	20	1
S17	60	1	S58	25	1	S99	19.3	1
S18	77	0.7	S59	100	1	S100	20	1
S19	25	1	S60	60.4	0.2	S101	84.2	1
S20	86.7	1	S61	60.4	0.2	S102	40	1
S21	67.6	1	S62	73	1	S103	43.8	1
S22	60	1	S63	60.4	0.2	S104	28	1.66
S23	25	1	S64	60.4	0.2	S105	25.2	1
S24	35	1	S65	92	1.5	S106	25.5	1
S25	35.3	1	S66	92	1.5	S107	25.2	1
S26	35.3	1	S67	92	1.5	S108	25.2	1
S27	35.3	1	S68	85	1	S109	25.2	1
S28	25	1	S69	60.4	0.2	S110	76.6	0.4
S29	27.2	1	S70	92	1.5	S111	67	1
S30	25	1	S71	92	1.5	S112	25	1
S31	25	1	S72	92	1.5	S113	65	1
S32	25	1	S73	84	1	S114	41	1
S33	252.1	1	S74	102.2	1	S115	20	1
S34	252.1	1	S75	37	1	S116	20	1
S35	34.8	1	S76	37	1	S117	41	1
S36	42.5	1	S77	37	1	S118	41	1
S37	90	1.1	S78	118.9	1	S119	20	1
S38	90	1.1	S79	60	1	S120	20	1
S39	90	1.1	S80	130	0.4	S121	40.8	1
S40	53.2	0.18	S81	130	0.4	S122	41	1
S41	58.1	0.18	S82	130	0.4	S123	41	1

Table B.4 : Aspen Plus simulation software stream temperatures and pressures for CS-2 (S124-S224).

Stream No	Tem. (^{0}C)	Pres. (atm)	Stream No	Tem. (^{0}C)	Pres. (atm)	Stream No	Tem. (^{0}C)	Pres. (atm)
S124	41	1	S165	36.9	0.7	S207	535.3	1
S125	40.7	1	S166	223.9	0.29	S208	950	1
S126	40.7	1	S167	223.9	0.29	S209	950	1
S127	40.7	1	S168	223.9	18.43	S210		
S128	41	1	S169	282.4	0.21	S211	220	1
S129	41	1	S170	282.4	0.21	S212	25	1
S130	41.1	1	S171	107.4	0.21	S213	27.8	1
S131	40.8	0.7	S173	282.4	7.99	S214	219	1
S132	39.2	0.7	S174	84.2	1	S215	25	1
S133	41.1	1	S175	84.2	1	S216	25	1
S134	78.8	1	S176	99.8	1	S217	25	1
S135	80.9	3	S177	23	1	S218	25	1
S136	55.4	1.86	S178	60.5	0.2	S219	107	1.28
S137	102.5	1.91	S179	35	0.2	S220	108.2	42.33
S138	118.2	2.1	S180	20	1	S221	108.2	42.33
S139	41.2	1	S181	35	0.2	S222	348.8	42.33
S140	25	1	S182	35	1	S223	348.8	42.33
S141	35.9	0.7	S183	35	1	S224	122	2.08
S142	93.2	1.7	S184	35	1			
S143	120.7	2	S185	20	1			
S144	114.8	1.7	S186	25	1			
S145	114.8	1.7	S187	21.1	1			
S146	114.8	1.7	S188	21.1	1			
S147	38	1	S189	21.6	1			
S148	35	1	S190	21.1	1			
S149	117	2	S191	21.1	1			
S150	117	0.38	S192	21.1	1			
S151	117	1.77	S193	21.1	1			
S152	117	0.38	S194	21.1	1			
S153	70	0.38	S195	21.1	1			
S154	70	3.2	S196	21.1	1			
S155	70	3.2	S197	21.1	1			
S156	70	3.2	S198	21.1	1			
S157	25	1	S199	100	1			
S158	70	3.2	S200	100	1			
S159	120.7	2	S201	25	1			
S160	25	1	S202	21.1	1			
S161	388.3	9.51	S203	31.8	0.21			
S162	40	9.51	S204	950	0.99			
S163	68.9	3.2	S205	25	1			
S164	68.9	3.2	S206	25	1			

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EDUCATION:

B.Sc. : 2009, Chemical Engineering Department
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B.A : 2011, Business Management, Department of Management & Organisation, Anadolu University.

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INTERNATIONAL EXPERIENCES

July, 2010 – January, 2011 : Visiting Scholar, Biological and Agricultural Department, University of Idaho, Moscow, Idaho/USA

PROFESSIONAL EXPERIENCES

September, 2009 – Present **:** Research and Teaching Assistant
Energy Systems Engineering Department
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SCHOLARSHIPS

July, 2010 – October, 2010 **:** YOK (The Council of Higher Education),
International Research Scholarship,
Visiting Scholar

2002 – 2004 **:** Bursa Ozel Çekirge Dershanesi Achievement Grant

PUBLICATIONS/PRESENTATIONS ON THE THESIS

- **Borand, M.N,** Karaosmanoglu, F. (2018), "Effects of organosolv pretreatment conditions for lignocellulosic biomass in biorefinery applications: A review", Journal of Renewable and Sustainable Energy, 10(3), 033104-23, doi: 10.1063/1.5025876 (Total citations: 4)

- **Erdönmez Borand, M., N.,** İşler, A., Karaosmanoğlu, F., "Review: Comparison of Pretreatment Methods for Bioethanol Production", World Renewable Energy Congress 2013, Murdoch University, Perth-Australia, July 14-18, 2013. (Oral presentation)

- **Erdönmez Borand, M.N.,** İşler, A., Karaosmanoğlu, F. "Economical and Environmental Life Cycle Analysis For Bioethanol", 37th IAEE International Conference: Energy & The Economy, Newyork-USA, June 15-18, 2014. (Oral presentation)

PROCEEDINGS

National Proceedings

- Başakçılardan Kabakcı, S., **Erdönmez Borand, M., N.,** "Development of Renewable Energy Education Curriculum in Vocational High Schools: ALPER Project", 9th National Clean Energy Symposium, Konya, December 25-28, 2013.

International Proceedings

- **Erdönmez, M., N**., İşler, A., Karaosmanoğlu, F., "The Current Situation of Engine Fuels in Turkey", ASABE Bridges to Sustainable Agriculture Conference, Lethbridge-Canada, September 9-11, 2010.

- Jain, T., Deis, B., **Erdönmez, M., N.**, Van Gerpen, J, Feris, K., "Enzymatic Conversion of Lignocellulosic Biomass to Sugars", ASABE Bridges to Sustainable Agriculture Conference, Lethbridge-Canada, September 9-11, 2010.

- **Erdönmez Borand, M., N.,** Karaosmanoğlu, F., Van Gerpen, J, "Effects of Ball Mill Pretreatment on Sugar Determination From Lignocellulosic

Biomass”, Bioenergy From Forest 2012 Conference, Jyvaskyla-Finland, August 27-29, 2012.

- **Erdönmez Borand, M., N.,** İşler, A., Karaosmanoğlu, F., Van Gerpen, J, “Effective Lignocellulosic Bioethanol Production: Combined Pretreatment Methods”, 23rd European Biomass Conference and Exhibition (EUBCE), Vienna/Austuria, June 1-4, 2015.

CERTIFICATIONS

- “Data Analysis for Excel”, Bilge Adam Information Technology Academy Microsoft Office Educations, Istanbul Technical University Chemical Engineering Club Courses, March 28-30, 2006.
- “Project Management Training”, P&G Gebze Plant, Istanbul Technical University Chemical Engineering Department Courses, Istanbul, November 13, 2008.
- “Energy Efficiency in Buildings Training”, EUBuild Project is implemented by Association of Turkish Construction Material Producers (IMSAD), Istanbul, March 5, 2009.
- “Energy Efficiency Capacity Building Programme on EU Legislations, Financial Tools, EE in Municipalities and EE Action Plan” Heinrich Böll Stiftung Foundation Turkey Representative, Ankara, March 23-25, 2011.

PROJECTS

National Projects

- **Borand M. N.,** Researcher, EU Sustainable Energy Week (EUSEW-ASEH), “Training of Energy Trackers”, Project of Yalova University Energy Systems Engineering Department, 2010.
- Karaosmanoğlu, F., **Borand M. N.,** Researcher, “Bioethanol Production from Industrial Woody Biomass, Plant Design, Environmental and Economical Life Cycle Analysis: A Case Study from Bursa/Turkey Region” ITU Scientific Research Project, November 2013-November 2015.

International Projects

- **Borand M. N.,** Researcher, "ALPER-Adapting Learning Programme for Energies of Renewable", EU-Leonardo da Vinci Project-Transfer of Innovation, 2011-2014.
- **Borand M. N.,** Researcher, “WASTENET-A Black Sea Network Promoting Integrated Natural Wastewater Treatment Systems”, EU-Black Sea Cross Border Cooperation, 2013-2015.

REVIEWER

- Journal of Renewable and Sustainable Energy
  https://aip.scitation.org/journal/rse
  (2018-present)

- Applied Energy
  https://www.journals.elsevier.com/applied-energy
  (2019-present)

ASSISTED COURSES in 2018-2019 ACADEMIC YEAR

- Energy systems engineering laboratory 2
- Energy systems engineering laboratory 1
- General chemistry
- General chemistry laboratory
- Mass and energy balances
- Renewable energy sources
- Occupational health and safety
- Energy efficiency in buildings

ADMINISTRATIVE DUTIES

- Publicity and communication committee (2018-present)
- Coordinator of energy systems engineering laboratory (2017-present)
- Course plan-schedule-exam committee (2016-2018)
- Alumni committee (2014-2016)

DUTIES IN SCIENTIFIC ORGANIZATIONS

- Head of Student Chapter, Turkish Association for Energy Economics (2015 - 2018)
- Youth Committee Member, VI. Istanbul Carbon Summit: Carbon Management, Technologies & Trade, Istanbul Technical University, Suleyman Demirel Cultural Center, April 9, 2019.
- Organization Committee Member, 38th IAEE International Conference: Economic, Environmental, Technological And Security Challenges for Energy, Antalya/Turkey, May 25-27, 2015.
- Youth Committee Member, II. Istanbul Carbon Summit: Carbon Management, Carbon Technologies and Carbon Trading, Grand Cevahir Hotel, April 2-3, 2015.
- Youth Committee Member, I. Istanbul Carbon Summit: Carbon Management, Carbon Technologies and Carbon Trading, Istanbul Technical University, Suleyman Demirel Cultural Center, April 3-5, 2014.

PROFESSIONAL MEMBERSHIP

National Membership

- Sustainable Production and Consumption Association (SUT-D)
- Turkish Association for Energy Economics (EED)

International Membership

- International Association of Energy Economics (IEED)

SOCIAL MEMBERSHIP

- ITU Chemical Engineering Club (2005-2008)
- CMAS 1 Star Diver (2014-present)