Process Synthesis and Design of Integrated Biorefinery in Pulp and Paper Industry

Miss Ghochapon Mongkhonsiri

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Engineering in Chemical Engineering
Department of Chemical Engineering
FACULTY OF ENGINEERING
Chulalongkorn University
Academic Year 2019

การสังเคราะห์ และออกแบบการบูรณาการกระบวนการไบโอรีไฟเนอรี่ในอุตสาหกรรมเยื่อและกระดาษ

น.ส.กชพร มงคลศิริ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรดุษฎีบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2562

Thesis Title	Process Synthesis and Design of Integrated Biorefinery in Pulp and Paper Industry
By	Miss Ghochapon Mongkhonsiri
Field of Study	Chemical Engineering
Thesis Advisor	Professor Suttichai Assabumrungrat, Ph.D.
Thesis Co Advisor	Assistant Professor Pomthong Malakul, Ph.D. Professor Rafiqul Gani, Ph.D.

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in Partial Fulfillment of the Requirement for the Doctor of Engineering

-- Dean of the FACULTY OF ENGINEERING
(Professor SUPOT TEACHAVORASINSKUN, Ph.D.)

DISSERTATION COMMITTEE

-- Chairman
(Associate Professor Tawatchai Charinpanitkul, Ph.D.)

-- Thesis Advisor
(Professor Suttichai Assabumrungrat, Ph.D.)

-- Thesis Co-Advisor
(Assistant Professor Pomthong Malakul, Ph.D.)

-- Thesis Co-Advisor
(Professor Rafiqul Gani, Ph.D.)

-- Examiner
(Associate Professor Varong Pavarajarn, Ph.D.)

-- Examiner
(Assistant Professor Sorada Kanokpanont, Ph.D.)

-- External Examiner
(Pongsuda Pongtanya, Ph.D.)

กชพร มงคลศิริ : การสังเคราะห์ และออกแบบการบูรณาการกระบวนการไบโอรีไฟเนอรี่ใน อุตสาหกรรมเยื่อและกระดาษ. (Process Synthesis and Design of Integrated Biorefinery in Pulp and Paper Industry) อ.ที่ปรึกษาหลัก : ศ. ดร.สุทธิชัย อัสสะบำรุงรัตน์, อ.ที่ปรึกษาร่วม : ผศ. ดร.ปมทอง มาลากุล ณ อยุธยา,ศ. ดร.ราฟิค กานี่

ระบบการบูรณาการไบโอรีไฟเนอรี่เข้ากับอุตสาหกรรมเยื่อและกระดาษถูกพิจารณาว่าเป็นการพัฒนาอย่างยั่งยืนสำหรับอุตสาหกรรมเยื่อและกระดาษและกระบวนไบโอรีไฟเนอรี่ด้วยวัสดุลิกโนเซลลูโลส การผลิตสารเคมีชีวภาพมูลค่าสูง เชื้อเพลิงชีวภาพ และ พลังงานชีวภาพถูกดำเนินการร่วมกับโรงงานผลิตเยื่อที่มีอยู่แล้ว โดยการบูรณาวัตถุดิบและสาธารณูปโภค ระเบียบวิธีการอย่างเป็นระบบซึ่งใช้การสังเคราะห์กระบวนการด้วย โครงสร้างขนาดใหญ่ การออกแบบกระบวนการ และนวัตกรรมเป็นวิธีการที่มีประสิทธิภาพเพื่อระบุแนวทางที่มีศักยภาพความยั่งยืนทั้งทางด้านเศษฐศาสตร์ และผลกระทบต่อสิ่งแวดล้อมโดยได้รับการสนับสนุนจากเครื่องมือที่ใช้คอมพิวเตอร์ช่วย โครงสร้างขนาดใหญ่ของโครงข่ายกระบวนการไบโอรีไฟเนอรี่หลายผลิตภัณฑ์กับอุตสาหกรรมเยื่อและกระดาษถูกพัฒนาและหาแนวทางที่เหมาะสมด้วยจุดประสงค์เพื่อให้ได้ผลกำไรสูงสุด ผลการสังเคราะห์กระบวนการฉายภาพการบูรณาการไบโอรีไฟเนอรี่ร่วมกับโรงงานเยื่อและกระดาษที่เหมาะสมสำหรับการออกแบบต่อไป การออกแบบกระบวนการและการประเมินให้ข้อมูลเชิงลึกที่เป็นประโยชน์เพื่อประเมินประสิทธิภาพของกระบวนการและระบุจุดอ่อนของกระบวนการเพื่อปรับปรุงโดยใช้นวัตกรรม ทางเลือกที่สะอาดกว่า โดยใช้การนำคาร์บอนไดออกไซด์มาใช้ในการสังเคราะห์เมทานอล และพลังงานแสงอาทิตย์ถูกพิจารณาสำหรับนวัตกรรมของกระบวนการเปรียบเทียบกับกรณีพื้นฐาน ระบบการบูรณาการไบโอรีไฟเนอรี่เข้ากับโรงงานเยื่อที่มีอยู่แล้วถูกพิสูจน์ว่าสามารถยกระดับศักยภาพของผลกำไร และผลประโยชน์ทางด้านสิ่งแวดล้อมเหนือโรงงานเยื่อดั่งเดิม และส่งเสริมผลิตภัณฑ์ชีวภาพเพื่อสังคมที่ยั่งยืน

สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2562

ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

5771401721 : MAJOR CHEMICAL ENGINEERING

KEYWORD: Biorefinery, Pulp and paper industry, Process synthesis, Process design

Ghochapon Mongkhonsiri : Process Synthesis and Design of Integrated Biorefinery in Pulp and Paper Industry. Advisor: Prof. Suttichai Assabumrungrat, Ph.D. Co-advisor: Asst. Prof. Pomthong Malakul, Ph.D.,Prof. Rafiqul Gani, Ph.D.

Integration of biorefinery into pulp and paper industry has been considered as sustainable development for pulp and paper industry and lignocellulosic biorefinery. High value-added biochemical, biofuel and bioenergy productions could be implemented into existing pulp mills by material and utility integration. A systematic methodology employing a superstructure-based process synthesis, process design and innovation is an effective approach to explore potential pathways for both economic and environmental sustainability with support from computer-aided tools. A superstructure of the multi-product biorefinery process network with the pulp and paper industry is developed and optimized with the objective to maximize profit. The synthesis results project the optimal integrated biorefinery combined with pulp and paper mills for further design. Process design and evaluation provide useful insights to assess the process performance and define process weakness for improvement by innovation. The cleaner alternatives implementing the CO_2 utilization via methanol production and solar energy is considered for process innovation comparing to the base case. Integrated biorefinery systems into the existing pulp mill is proven that can potentially enhance profitability and environmental benefit beyond conventional pulp mill and promote bioproducts for sustainable society.

Field of Study:	Chemical Engineering	Student's Signature ....
Academic Year:	2019	Advisor's Signature ....
		Co-advisor's Signature ....
		Co-advisor's Signature ....

ACKNOWLEDGEMENTS

I take this opportunity to express my sincerely gratitude to every support for this thesis. This work is financially supported by the Thailand Research Fund (DPG5880003), the NSTDA Chair Professor Grant (No.5) funded by the Crown Property Bureau of Thailand and National Science and Technology Development Agency, and the Royal Golden Jubilee Ph.D. Program from the Thailand Research Fund and Chulalongkorn University.

First, Professor Suttichai Assabumrungrat, I am truly appreciated your attempt and continuous support me to be the better one. I don’t have enough words to express my gratitude. I believe that I could not get good work without you. I learned so much from you and I will take your advice with me. You provided a great chance and invaluable experiences in my life. Thanks a million for everything you have done for me, Professor.

Also, I am so grateful to Professor Rafiqul Gani. I am honored to have your advice, suggestion, and recommendation. At DTU (Denmark), I learned a lot of things both about my Ph.D. Project and the different worlds that I have never known. Your advice takes me to have good works and be better. You support me so far. Thank you so much, Professor.

Moreover, Thank you for useful recommendations and comments of all committees.

Besides, I would like to thank both of you, Dr. Pongtorn Charoensuppanimit and Assistant Professor Amata Anantpinijwatna, to help me have good publications without outlandish grammar. Without you, I think I need much more time to get good papers. Thank you for your attempt.

Thank you, P’Math (Dr. Amata), P’Pim (Dr. Prathana) and P’Yui (Dr. Sawitree), for your help and suggestion. I really was fun and happy with you in Denmark. I will never forget the enjoyable moment. Thank you again for taking care of me, brother & sister.

Thank you, my friends. You are always by my side. Thank you for every talk that always encourages me.

Thank you for all of the researches that I have reviewed. I learned from them. We

have done it together.

Last but not the least, I would like to give a big hug to thank my family: my mother, father, and brother. I do love you. You are the wind beneath my wings. I hope I will be that wind for you too. Thank you every time with you.

Thank you for everything in both hard time and good time to make it happen!!

Ghochapon Mongkhonsiri

TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

CHAPTER 1

INTRODUCTON

1.1 Rationale

The climate change has drawn great attention from our society due to the progressively increased level of greenhouse gases in the atmosphere from fossil fuels utilization. In addition, the immense consumption of fossil fuels has contributed to diminishing fossil fuel reserves (Farhad et al., 2008). Sustainable and renewable sources of energy and chemicals have been developed for replacing fossil fuels. Biomass is a prominent source due to a carbon-neutral renewable resource and abundant quantity compared with the diminishing fossil fuels. For this reason, biomass is considered as an alternative sustainable source instead of petroleum (Yuan et al., 2013). Biomass can be used as a renewable feedstock to produce various value-added products involving biofuels, biochemical and biomaterials, also subrogating petrochemical products, though biorefinery processing. Biorefinery concept has been of considerable interest from around the world as a biomass conversion can lead to a spectrum of marketable products and energy, analogous to petroleum refinery. The concept of the petroleum refinery is useful for developing the biorefinery. Crude oil is normally a raw material of petrochemical industry, while for biorefinery is wood/biomass considered as renewable materials. The International Energy Agency Bioenergy Task 42 on Biorefineries has defined biorefining (Cheruini, 2010) as “the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, and materials) and bioenergy (biofuels, power and/or heat)”. The biorefinery has also been defined as a “facility integrating biomass extraction and conversion processes and equipment to produce fuels, power, heat, and value-added chemicals” by the National Renewable Energy Laboratory (NREL). An integrated biorefinery design would play a key role for providing sustainable supply of biofuels, biochemical and biomaterials good impacts on economics, environment and society.

Nowadays, biofuels and biochemicals are mostly produced from crops identified as first generation biorefinery. The first generation usually refers to biorefinery applying raw materials in competition with food and feed industries. For the first generation biorefinery, increasing price of crude oil will contribute to increasing food price and land use problem since a larger proportion of agriculture will be dedicated to biofuels and biochemicals production instead of food production. This problem is the cause of developing the second generation biorefinery. At second generation as a possible greener alternative, non-food biomass is used as raw material, especially lignocellulosic including agricultural residue and forestry biomass. The potential of implementing any biorefinery is evaluated in term of available feedstock, applicable technological processes and market demand trends. Forestry biomass provides remarkable feedstock for biorefineries when integrated into a pulp and paper mill because of its availability, especially non-competition with agricultural crops for fertile land (Cherubini, 2010).

The pulp and paper industry today is the world's largest non-food biomass utilization system and a huge user and producer of bioenergy and biomaterials. Nowadays, the printing paper consumption has been declining due to replacement by digital media such as tablet, computer, laptop computer and smart phone. Moreover, the pulp and paper industry is characterized by high investment, mature markets of several core products, low innovation development and increasingly international firms operating in global markets with high price volatility. The traditional pulp and paper industry needs to transform for responding to the current situation, increased competition and changes in consumption habits (Kouhia et al., 2015). How to materialize a transformation towards a low-carbon bio-economy as well as realize the necessary new green innovations is the current key challenge of the pulp and paper industry breakthrough (Pätäri et al., 2016). Bio-economy defined by European Union (EU) (Dries et al., 2016) is “encompassing the sustainable production of renewable resource from land, fisheries and aquaculture environments and their conversion into food, feed, fiber, bio-based products and bioenergy as well as the related public goods. It includes agriculture, forestry, fisheries, food and pulp and paper production, as well as parts of chemical, biotechnological and energy industries”. To improve financial performance and competitiveness, the currently operating pulp and paper mills should look over their business models to take in new revenue stream from an expanded product portfolio. Implementing biorefinery activities into an existing pulp and paper mills has received much attention as an opportunity for new revenues generation from new value-added products (Marinova et al., 2009). The integrated biorefinery network is considered as the sharing of raw materials, by-products, utilities, and infrastructure with the existing mill causing significant economic and environment advantages. The current pulp and paper mills mainly convert wood, chemicals and energy into pulp and paper products. Towards the purpose of the efficiency and profitability improvement, the integration of biorefinery into traditional pulping process will be generated to transform simply manufacturing of low-margin paper into marketable multi-products by integrated production of bioenergy, biofuels and biochemicals. The novel network of integrated biorefinery into the existing pulp mill has been considered as a future pathway for long-term sustainable growth of biorefinery and paper industry by many advantages; higher efficiency of raw material utilization, protection of traditional product lines, creation of higher skilled and better paying jobs, and access to new domestic and international markets for bioenergy and biochemical (Ulrika & Paul, 2006). Comparison of the basic material streams from a today’s pulp and paper mill and the possible material streams for a future biorefinery mill in addition to pulp and paper production are illustrated in Figure 1.

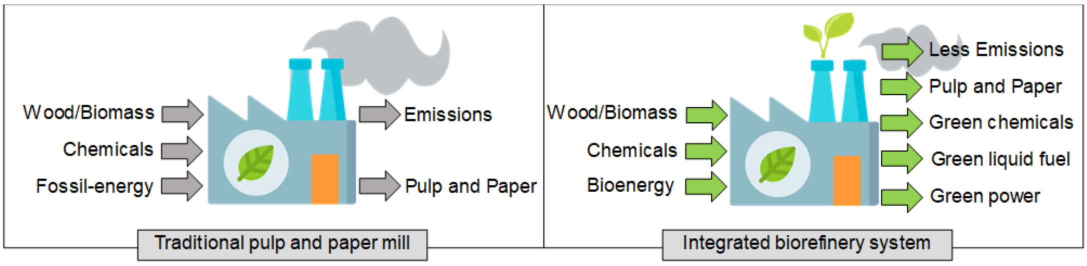


Figure 1 Schemes of traditional pulp and paper mill and a future's Integrated Biorefinery System with pulp and paper mill

The concept of green forest biorefinery integrated into a Kraft mill was proposed by Maryam et al (2013). It is said that a combining site of specialty wood pulp and bio-product, biomass gasification, power cogeneration and optimal absorption heat cycles for heat upgrading is attractive for pulp and paper improvement. Moreover, the mature pulp and paper industries can be potentially transformed into more diversified and profitable businesses by integrating biorefinery technologies. However, the transformation pathways, product mix, suitable conversion technologies, market uncertainty evaluations, and sustainable development are still considered as challenges that must be undertaken. Successful transformation will require progressive implementation of new business plans by generating the new technologies with minimizing the risks and increasing profitability. The sustainability of development depends on the successful implementation of intensive energy and mass integration and optimization criterion.

In 2014, Rafione and colleagues introduced a new concept, the Green Integrated Forest Biorefinery (GIFBR) with a zero fossil fuel based on an existing Canadian Kraft pulping mill (Rafione et al., 2014). Due to environmental and economic concerns, the aim of zero fossil fuel consumption has been of interest. Nonetheless, development of the concept is complex. The intensity of mass and energy integration between biorefinery unit and existing pulping process has to be assessed to optimize the overall energy requirement and assure no fossil fuel usage. Their process configuration included a furfural production as biorefinery unit, also implemented gasification and poly-generation unit as energy supplier with an existing pulp mill. They reported that this integrated process development is difficult to determine the achievement level of sustainable integration between the receptor pulp mill and the biorefinery unit. Their goal is self-sufficient energy consumption of a green integrated biorefinery. The proposed Green Integrated Forest Biorefinery (GIFBR) aspects are low greenhouse gases emissions, reduced water consumption, production of effluents and especially no fossil fuel usage. This proposed configuration is technically and economically feasible. However, they recommended that the investment of such integrated facilities should be divided over the years to spread the investment cost and reduce the risks.

Integrated Biorefinery System involves implemented biorefinery units and an existing pulping mill as mature receptor. Typically, a chemical pulping process is particularly an appropriate receptor for fractionation of lignocellulose because parts of lignin and hemicellulose, traditionally burnt to recover digesting chemical agent and energy content, can be extracted and used as biorefinery raw materials, whereas, paper pulp is a cellulosic fiber, conventionally used for paper and packaging. Via implementing of biorefinery technologies, these pulping products and by-products have more potential for production of high value bio-products apart from conventional pathway. There are still significant challenges related to these new technologies, but a numerous of them have been looked as promising alternative. The conversion of biomass is accomplished by various extraction and transformation pathways, which contribute to the opportunity to revitalize the pulp and paper industry. New technologies that can be integrated into an existing pulp and paper mill, transforming it into a success Integrated Biorefinery System, need to be established and evaluated in economic, environmental and social feasible before commercial investment. However, study on synthesis and design of biorefinery technologies network that have potential for integration into existing pulp and paper mill are not still enough for commercial development of integrated forest biorefinery. Overview of possible integrated biorefinery pathways has been detailed obviously. Most studies have focused on the development of methodology for integrated biorefinery design.

Bio-products, produced via biorefinery process, mainly vary with type of feedstocks available (Towers et al., 2007). Characteristics of feedstock such as cost, composition, location, moisture content, and availability define the suitable biorefinery technical options. Each biorefinery option contains a unique and/or novel technology which might posture technological, market and environmental risks to any mill under different consideration. The selection and implementation of biorefinery technology is complex that depends on several factors such as local market supply chains, price of electricity, availability and need for cheap fuels, cost of transportation, possible energy integration, size of mill, carbon trading, etc. Selecting the wrong biorefinery configuration leads to financial disaster. Therefore, it is critical that energy-efficient and cost-effective biorefinery design strategies and effective evaluation tools are developed for optimal allocation of resources including biomass, energy, utilities, water, and chemical reactants (Benali et al., 2014). Emerged biorefinery technology as a retrofit unit must be precisely considered to understand the impact on existing processes, e.g., pulp yield reductions because carbon is used to convert into alternative products, and black liquor change in quantity and quality. Apart from process technology development, market trend and value of biorefinery products, and their supply chain management strategies are also vital for successful development (Bajpai, 2011). These factors are different for each mill therefore the biorefinery unit to be implemented in this retrofit context varies from site to site. The best pathway for the Integrated Biorefinery System is complex and specific in each site (Ulrika & Paul, 2006). In practice, it is difficult to address all these decision within a single supply chain optimization model. A systematic hierarchical methodology may be suitable for addressing all these factors in a step wise manner. There is the development of feasible and practical biorefinery strategies that a company can strategically obtain. Nevertheless, it has not been such a methodology which can identify a global optimum. The overall possible implementing of biorefinery technologies as alternative superstructure of Integrated Biorefinery System based on pulp and paper mill as the key knowledge of the development has never been generated and studied. The superstructure can be modeled and optimized to find the best pathway for conditions, location and criterion of each company. Economic, social and environmental feasibility must be evaluated for sustainability. Essentially, superstructure-based systematic methodology supported with computer aided tools should be applied to synthesize and design the sustainable Integrated Biorefinery System from generated alternative superstructure. The superstructure of Integrated Forest Biorefinery technologies as all possible alternative pathways can be used as starter to find the best pathway of any resemble mill. Based on the superstructure optimization, the promising system can be performed further process evaluation as well as hot-spot analysis to induce process innovation for more sustainable development.

For Thailand, because pulp and paper business has a growing competition from China and other countries around the world, the paper exports and market share decline. Moreover, the consumer demand for printing and writing paper decreased and customers turn to use more paper packaging. To develop sustainable business and stepped up competition from around the world, improving financial performance, competitiveness and environmental problem, the currently operating pulp and paper mills are looking over their business models to take in new sources of revenue from a diversified product portfolio. Integrated Biorefinery System into the existing mill should be applied. This study aims at identifying the promising integrated biorefinery network based on Thailand's context. The superstructure of alternatives is generated and proposed based on possible integrated biorefinery technology options from literature. Thailand's pulp and paper industry is studied as a case study that of for industry improvement. The optimum pathway for Integrated Biorefinery System into the Thailand's pulp and paper industry is proposed from generated superstructure optimization. It is evaluated by economic and environmental impacts and then designed for novel sustainable biorefinery process. A systematic methodology supported with computer aided tools is applied to synthesize and design Thailand's pulp and paper business transformation into a sustainable Integrated Biorefinery System.

1.2 Objective of study

To synthesize and design an optimal Integrated Biorefinery System with existing pulp and paper industry as sustainable alternatives for pulp and paper business in Thailand using a systematic methodology supported by a collection of computer aided tools.

1.3 Scope of works

1. The Integrated Biorefinery System (IBS) which involves implementing biorefinery units into existing pulping mill is synthesized based on Thailand's pulp and paper industry.
2. Superstructure of Integrated Biorefinery System is generated to represent process alternatives that is considered the traditional pulping process comparing to new technologies.
3. Superstructure of Integrated Biorefinery System includes alternatives of biorefinery technologies which are possibly integrated with existing pulp and paper mill by sharing raw materials, by-products, utilities and infrastructure.
4. Data for pulping process will be based on Thailand convention to get the process suitable for Thailand.
5. The optimization of Integrated Biorefinery System is obtained under generated superstructure. Technical and economic information that required for superstructure optimization was collected based on available data in public source. Economic data is applied by a single point.
6. The optimal integrated process is improved to achieve more sustainable network in term of economic or/and environmental assessment based on information from process design and evaluation.
7. The Integrated Biorefinery System is discussed for evaluating potential business transformation from current pulp and paper industry into a novel Integrated Biorefinery.

8. Estimation missing parameters from Aspen Plus® by using various properties methods and model is used for estimating thermodynamic properties of some components with missing thermodynamic properties (Gibb's free energy of formation) which are required for simulations of the process.

9. Simulation program Aspen Plus® and data from literature reviews is used to obtain data for evaluation of the energy consumption, economic and environmental impact.

1.4 Structure of Thesis

The thesis consists of 8 chapters. Chapter 1 is rationale of the research objective and scopes of work. Chapter 2 mentions about literature reviews of biorefinery technologies, pulping process, integration of biorefinery with pulping process and systematic framework for biorefinery development. Chapter 3 describes systematic methodology which was applied for process development of sustainable biorefinery. Chapters 4, 5 and 6 demonstrate the applications of systematic methodology to synthesize and design integrated biorefinery in pulp and paper process, following 3-stage framework of the methodology. Chapter 4 illustrates the first stage task (synthesis stage) at which an optimum biorefinery network integrated into pulping process is defined by superstructure-based process synthesis. Chapters 5 and 6 highlight process design and innovation of integrated biorefinery networks based on optimum pathway defined in Chapter 4 for Kraft and Soda pulping processes. Chapter 7 is conclusions and remarks to summarize the research results and key finding, also the suggestion is state in this chapter.

CHAPTER 2

LITERATURE REVIEW AND THEORY

In this chapter, the necessary information and principles of the Integrated Forest Biorefinery synthesis and design from literature review and other sources were described in 4 parts as follows; Biorefinery Concept, Chemical Wood Pulping Process, Emerging Biorefinery Process Options, Integrated Forest Biorefinery Implementation Strategy and Systematic framework for development of biorefinery-integrated system.

2.1 Biorefinery Concept

Biomass and petroleum are similar in their nature of complex compositions which could be extracted into main groups of appropriate substances. Its primary separated substances from subsequent processing and treatment lead to a wide range of products. In efficient product lines, the system is capable to produce a whole range of goods such as basic chemicals, intermediate goods, and sophisticated products. Biorefinery must adapt the principle of petroleum refineries to generate efficient product lines based on built family trees. In the future, Biotechnological conversion will play significant role in chemical production instead of traditional petrochemical conversion. Minimal consumption of non-renewable energy resources and environmental impacts with maximum efficient feedstock utilization is a key attribution to sustainable conversion processes. The American National Renewable Energy Laboratory (NREL) publishes the biorefinery definition: “A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today’s petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic bio-based industry”.

Today's biorefinery technologies are performed in two approaches: (1) the utilization of the whole plant or mixed biomass and (2) integration of traditional and modern processes for utilization of bio-based raw materials or transformation of traditional into modern processes. Most of the traditional bio-product plants are currently rendered in single production chains that are not corresponding to the biorefinery concept. Current biorefinery plants usually use feedstock in competition with the food and feed industry like crops contributing to business expansion limitation. On the other hand, lignocelluloses are non-food raw material that can reduce the competition for fertile land with food and feed feedstock. Moreover, biorefinery based on lignocellulosic feedstocks can rely on larger biomass per hectare yields since the whole plant is available as feedstock when comparing to conventional crops like corn or cassava that can use only a small fraction of the whole plant. The lignocellulosic feedstocks are mainly hemicellulose, cellulose and lignin can be converted into building block molecules, chemicals, fuels, polymers, or pulp. Large-scale operations of lignocellulosic biorefinery have potential as profitable and sustainable in the future (Bajpai, 2013).

The biorefinery's main processes for lignocellulosic can be divided into two different technology platforms including the "biochemical platform", and the "thermochemical platform" as mentioned in Table 1. The "two-platform concept" is biochemical platform which biomass composing, on average, of 75% carbohydrates are hydrolyzed to intermediate sugars as a basis of further conversion for biochemicals production, and the other is thermochemical conversion producing synthesis gas and its derivatives (Figure 2). The "biochemical platform" referred to as "sugar platform" is based on biological and chemical conversion processes and focuses on utilization of sugars extracted from biomass. The "thermochemical platform" some called "syngas platform" is referred to thermochemical conversion processes focusing on the gasification processes. In addition to the gasification, hydro-thermolysis, pyrolysis, thermolysis, and burning are also thermochemical conversion processes.

Table 1 Biorefinery platforms (Carvalheiro et al., 2008)

Platforms	Raw materials	Processes	Products	Status
Biochemical	• Lignocellulose • Starch • Sugar	• Chemical and enzymatic hydrolysis • Fermentation • Biotransformation • Chemical and catalytical processes	• Value added chemicals • Building block chemicals • Biomaterials • Biofuel • Heat • Electricity	• Laboratory • Large scale pilot plant • Commercial (ethanol fuel from sugar and starch based biomass)
Thermochemical	• Lignocellulose • Starch • Sugar • Plastics • Rubber	• Thermochemical processes O Gasification O Pyrolysis	• Syngas • Pyrolysis oil • Value added chemicals • Gaseous or liquid fuels	• Laboratory • Large scale pilot plant
Biogas	• Liquid effluents • Manure	• Anaerobic digestion	• Biogas (CH4&CO2) • Value added chemicals	• Large scale pilot plant • Commercial
Carbon-rich chains (Oil)	• Plant oil • Biodiesel • Animal fat	• Transesterification	• Fatty acid methyl ester (Biodiesel) • Glycerin • Fatty acids as platform chemicals	• Commercial

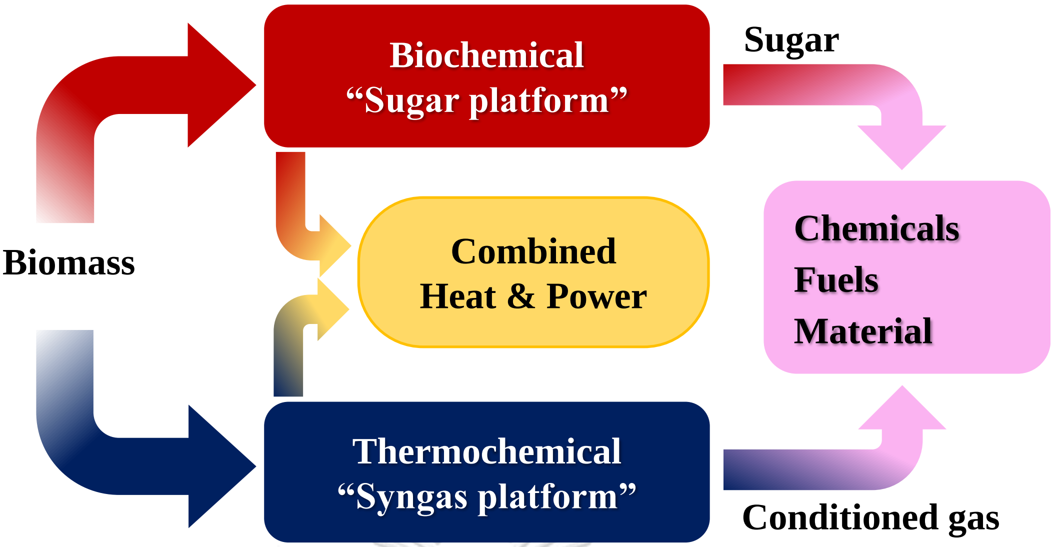


Figure 2 Two platform concept of biorefinery (Zafar et al., 2019)

2.1.1 Biochemical Platform

Biochemical platforms include an application of several extractions, separation, chemical conversion and biological conversion processes for biofuels and biochemicals production.

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin which can be converted to value added biochemicals via biological and chemical conversion as shown in Figure 3. Biomass in general consists of 40-50% cellulose, 25-30% hemicellulose and 15-20% lignin and other additive (Menon & Rao, 2012). The most important challenge of commercial biochemical production is economic competitiveness with petroleum refinery process. Thus, the performance of conversion process, productivity and yield of the desired product should be maximal while investment and operating cost are minimized (Choi et al., 2015). In 2004, the U.S. department of energy (DOE) selected top 10 chemicals that can be produced from biomass (Werpy & Petersen, 2004). Then in 2010, DOE updated the report based on the new criteria. Table 2 shows the comparison of top value added chemicals between 2004 and 2010 in DOE report. New biochemicals which have potentially growth were additionally included in this 2010 DOE's report where certain less growth market biochemicals were excluded (Bozell & Petersen, 2010). Top value-added biochemicals proposed by DOE can be produce from biomass via biological and chemical route illustrated in Figure 4.

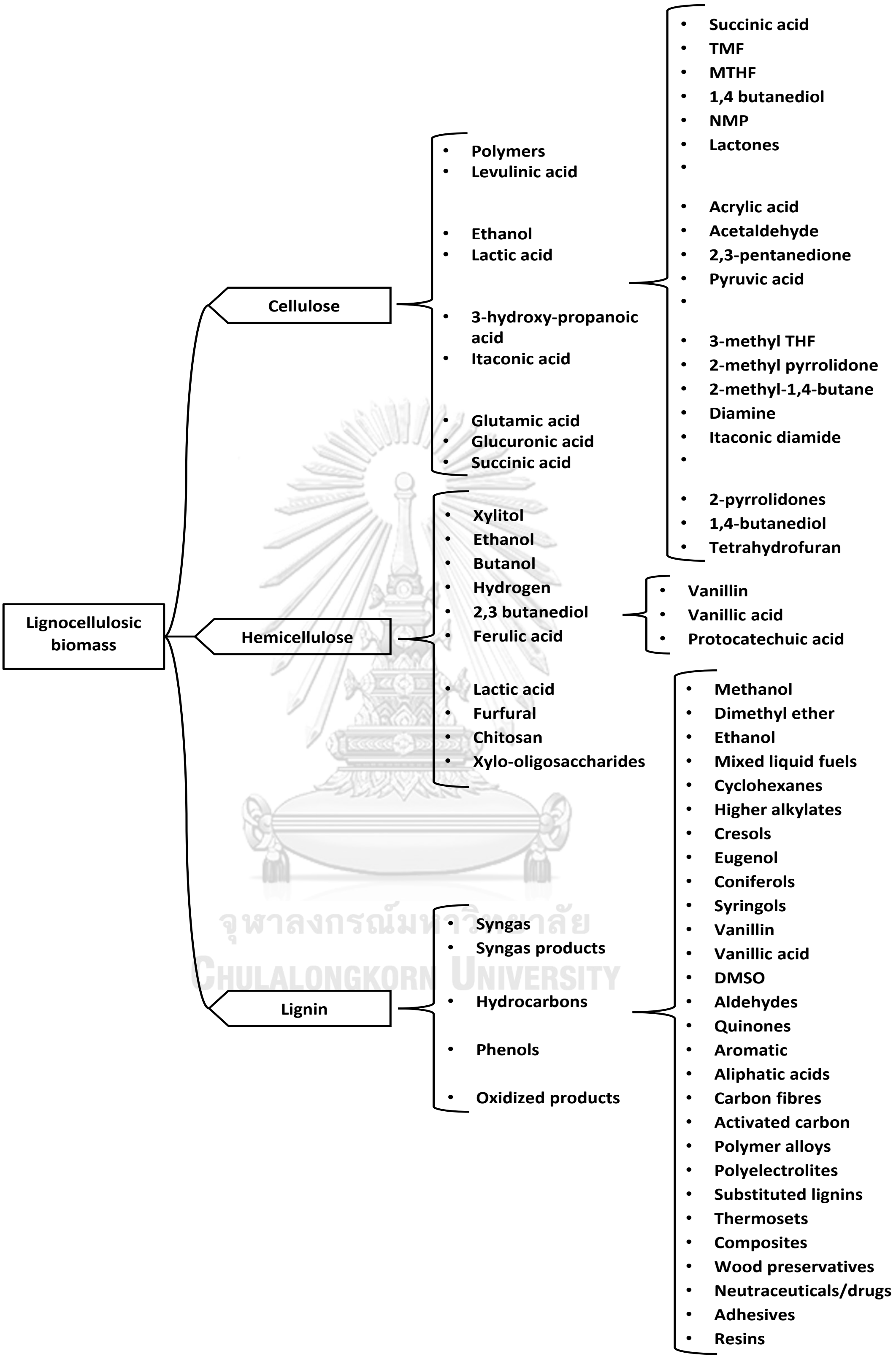


Figure 3 Value added biochemicals potentially derived from cellulose, hemicellulose and lignin (Menon & Rao, 2012)

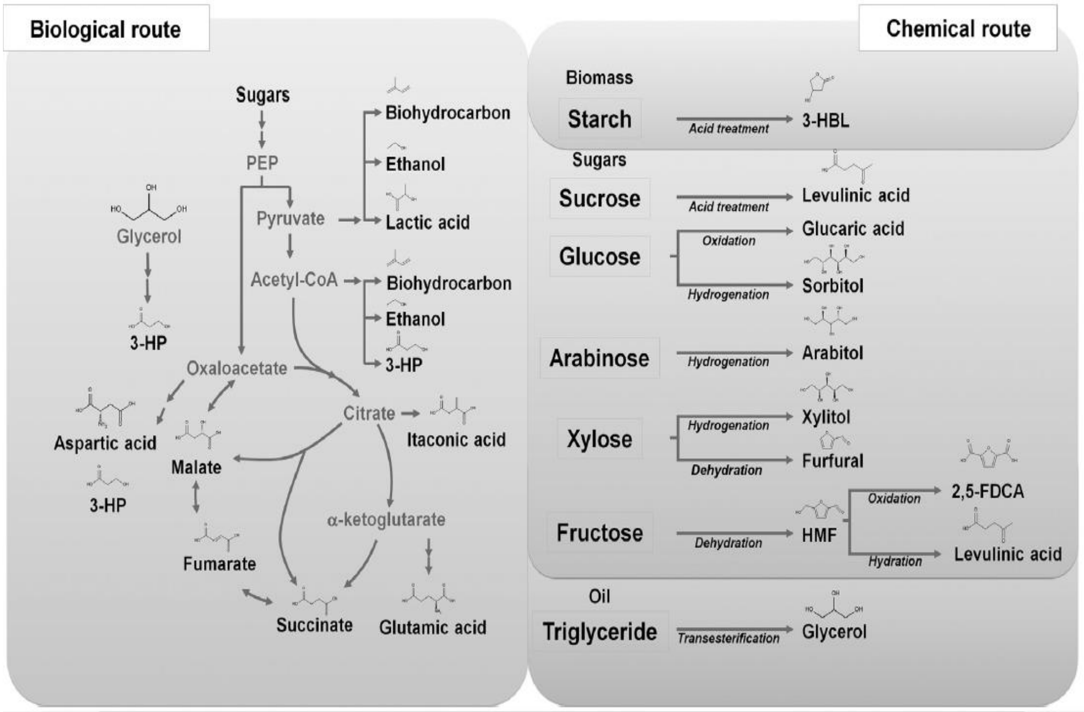


Figure 4 Biological and chemical routes for the production of DOE's top 12 biochemicals in 2004 and top 10 biochemicals in 2010 (Choi et al., 2015)

Table 2 "Top 10" bio-based chemicals in 2010 comparing to in 2004 by U.S. Department of Energy (Janssen, 2012)

Top value-added biochemicals (US DOE report)	
Year 2004	Year 2010
	Biohydrocarbons (isoprene, other)
	Lactic acid
	Ethanol
Succinic acid, fumaric and malic acid	Succinic acid
2,5 Furan dicarboxylic acid	Furans (Furfural, HMF, FDCA)
3-Hydroxypropionic acid	Hydroxypropionic acid/aldehyde
Levulinic acid	Levulinic acid
Glycerol	Glycerol and derivatives
Sorbitol	Sorbitol
Xylitol/arabinitol	Xylitol

Aspartic acid, glucaric acid, glutamic acid, itaconic acid 3-Hydroxybutyrolactone	

Five-carbon (C5) and six-carbon (C6) sugars are main components of wood and woody residues in a complex lignocellulosic matrix. A C5 sugar such as xylan is harder to ferment than the C6 sugars, like glucose. Thus, it is challenges to efficiently utilize C5 sugar by developing biomass pretreatment stage, sugar hydrolysis, and C5 sugar fermentation. Pretreatment configuration depends on the specific objective of biorefinery process either full conversion of biomass or pre-extraction of sugars in wood before Kraft cooking process.

In full conversion of biomass case, pretreatment step aims to enhance the accessibility of all components in the complex structure of lignocellulose. For Kraft processing case, a mild pretreatment is required to selectively extract hemicelluloses from wood to coproduce biofuel and biochemicals together with main pulp product (Walton et al., 2010). Hemicelluloses pre-extraction may generate more revenue stream for pulping industry. The main pretreatment processes include auto-hydrolysis, dilute acid hydrolysis, and steam explosion. After biomass pretreatment, there are several process alternatives both chemical and biological conversion to produce high value added biochemical leading to economic improvement but also more complexity. Biological technologies are mainly performed in commercial due to its economic and environment feasible. There are several biological technologies that have performed currently:

1. Separated hydrolysis and fermentation
2. Simultaneous saccharification and fermentation

3. Simultaneous saccharification and co-fermentation

4. Direct microbial conversion.

Each technology has its own advantages and disadvantages as well based on process criterion and objective.

2.1.2 Thermochemical Platform

The thermochemical platform is thermal treatment processes to produce syngas or bio-oil as a building block that their conversion is bioenergy, biofuels, and biochemicals. There are several thermochemical technologies such as biomass gasification, black liquor gasification, biomass pyrolysis or liquefaction, and carbonization, oils aqueous phase reforming. Either solid, as wood residues, or liquid, as black liquor, can be converted into a synthetic gas, composing mainly of CO and H_2 (Tower et al., 2007). There is potential of the synthesis gas conversion into power, liquid fuels and/or chemicals. Some of the products that can be obtained from the thermochemical biorefinery are shown in Figure 5. The main technological barriers, should be overcame, is the tare limitation and/or cleaning specifications of syngas.

The gasification system with a combined cycle power production unit provides higher power production efficiencies and lower greenhouse gas emissions. However, barriers of its commercial application are its high capital costs and large-scale operation. So, this option needs to be thoroughly assessed technical and economic feasible. In the simplest, syngas as a gasification product is burned in dedicated boilers or co-burned in coal, fuel, and recovery boilers. In pulp and paper industry, syngas can also be employed instead of fossil fuels in lime-kiln operation. In addition to, syngas upgrading to synthetic natural gas is also another way to improving thermal gas applications and adding syngas value.

The design of any process associated to both platforms is virtually unlimited depending on the purpose of design that can maximize environmental and economic advantages. Boundary between these two platform concepts cannot be defined, due to their many synergetic interactions. The best biofuels, biochemicals, and bioenergy production pathway depends on availability of raw material, technological know-how, regional policies, market regulations, and dynamics.

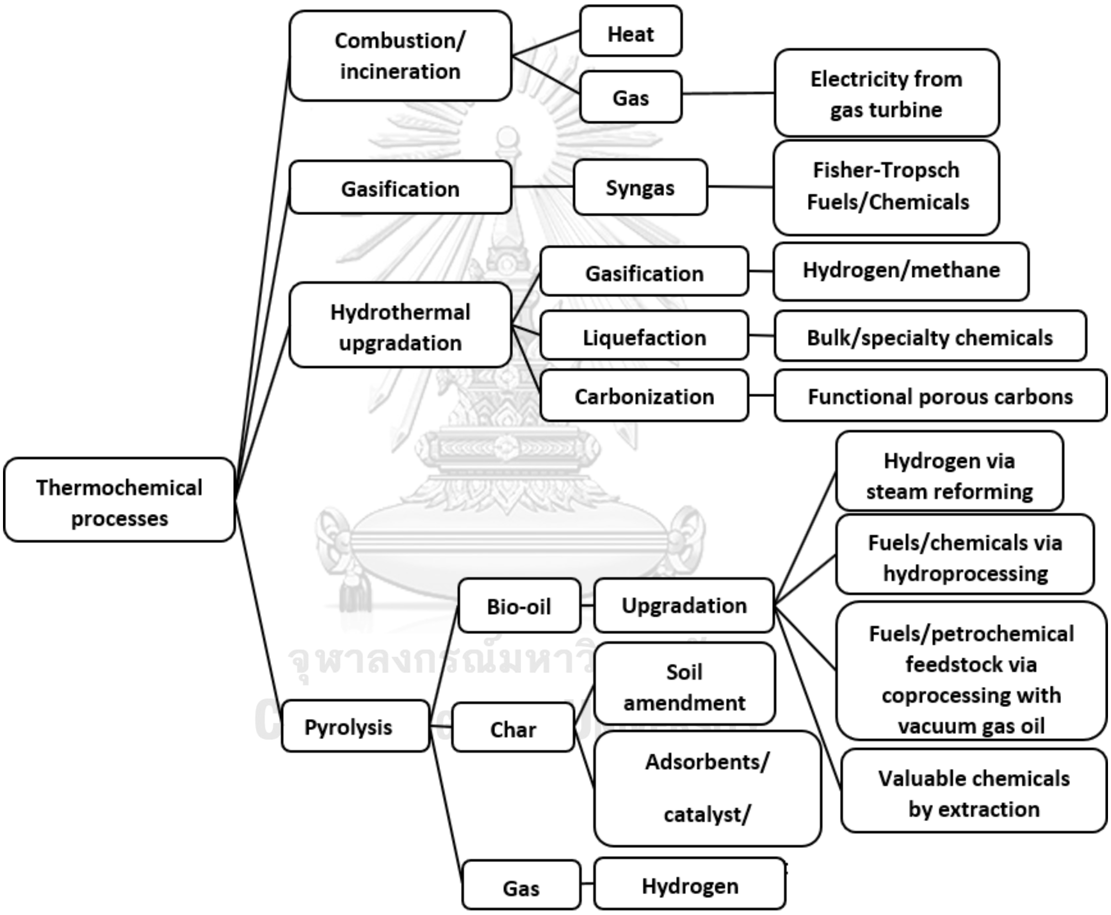


Figure 5 Thermochemical biorefinery pathways (Balagurumurthy et al., 2015)

2.2 Chemical Wood Pulping

Chemical wood pulping is a process for the extraction of cellulose from wood by dissolving the lignin in wood with chemical. The four of chemical pulping processes are Soda, Kraft, sulfite, and neutral sulfite semichemical (NSSC) processes. The first chemical pulping method patented in 1845 was Soda pulping process. Among these processes, Kraft process is the most popular pulping process for hardwood and softwood feedstock in industry (Agency & Standards, 1995).

2.2.1 Soda Pulping

Soda pulping process is one of the first chemical pulping methods using sodium hydroxide as the cooking chemical to get wood and non-wood pulp. Further, anthraquinone (AQ) can be used as a pulping additive to decrease the carbohydrate degradation and obtain more cellulose pulp. It is generally called Soda-AQ process. Soda pulp has lower tear strength than from Kraft and sulfite pulping processes. However, Soda process is appropriate for easy-pulped materials like non-wood, bagasse and straw, or some hardwoods. However, non-wood pulp shares 5-10% of the total chemical pulp produced in the world (Gea *et al.*, 2004). Soda process is commonly a commercial method in pulping of non-woody species.

In Soda pulping process, the feedstock is heated to 140-170°C and mixed with 13-16% sodium hydroxide in a pressurized cooking reactor. The Soda chemical is typically fed with ratio of liquid to dry feed at 5:1. In the cooking process, feedstock is digested when lignin is separated from the cellulose fiber as the solid phase and suspended in the liquid phase. The liquid phase called black liquor contains lignin and some of hemicellulose with cooking chemical. The solid phase containing liberated cellulose will be a pulp to further process to manufacture paper, boards, composite materials, packaging, polymers and so on.

The black liquor is typically sent to an evaporator and a recovery system to recover the sodium hydroxide for reuse in the pulping process. In the boiler, lignin in the thick black liquor is combusted for energy recovery while generating sodium oxide fly ash called green liquor. The Soda chemical is then recovered in the causticisation step where the sodium fly ash (i.e. sodium oxide) dissolves in water and reacts with calcium carbonate. Calcium oxide from the causticisation step can be also recovered to calcium carbonate by limekiln process. Soda pulping has the advantage that sulfur free lignin can be obtained. This is benefit for lignin utilization without sulfur-based gases. Moreover, silicic acid gel is possibly generated then increasing the revenue for the pulp mill by sale for special applications. The recovery operations are very efficient for pulping of softwood chips. Although the presence of silicate ions in non-wood material causes serious problems in the salt (e.g. sodium carbonate) and energy recovery from the black liquor, the Soda pulping process is still a predominant pulping process for non-wood biomass from agricultural by-products such as bagasse and straw. Currently, Wet Air Oxidation (WAO) and Direct Alkali Recovery System (DARS) with combustion in a fluidized bed becomes the most popular low cost avenues of chemical recovery in Soda pulp mill with non-wood feedstock especially bagasse (Doherty & Rainey, 2006).

2.2.2 Kraft Pulping

Kraft pulping process was developed after Soda pulping. It involves the combined use of sodium hydroxide and sodium sulfide as digesting agents. Kraft pulping dominates the chemical pulping industry. Following Figure 6, wood chips are digested with a water solution of sodium sulfide and sodium hydroxide called "white liquor" at elevated temperature and pressure. White liquor can chemically dissolve lignin from crystalline cellulose fibers.

There are two types of digester system: batch and continuous. At present, batch digester system is a more typical one, although the recent installations are mostly continuous system. In a batch digester, the complete cooking contents are transferred from digester to an atmospheric tank as a blow tank and next to pulp washers where “black liquor”, the spent cooking liquor, is separated from the pulp. The pulp may be bleached, before pressing and drying into the finished product. In contrast, continuous digester systems do not apply the "blow" of the digester.

Kraft process is designed for the cooking chemicals and heat recovery system. The mixture of spent cooking liquor and pulp washing water is removed from pulping line, as weak black liquor. It is further concentrated about 55% solids in a multiple-effect evaporator system and then to 65% solids in a direct-contact evaporator with the flue gases from the recovery furnace, or in an indirect-contact concentrator. The concentrated black liquor is then burned in a recovery furnace. The organics dissolved in the black liquor can fire to provide heat for process steam generation. However, many mills that require more steam consumption than steam production of the recovery furnace need to apply conventional industrial boilers burning coal, oil, natural gas, or bark and wood for supplementing steam. Inorganic chemicals in the black liquor collect as a molten smelt at the bottom of the furnace. Sodium sulfate in black liquor is converted to sodium sulfide. The smelt is dissolved in water to form “green liquor”, which is transferred to a causticizing tank. Green liquor is regenerated to white liquor with quicklime (calcium oxide) in causticizing tank. White liquor will be recycled to the digester system as cooking chemical again. For quicklime regeneration, a lime mud which precipitating from the causticizing process is calcined in a lime kiln to form quicklime.

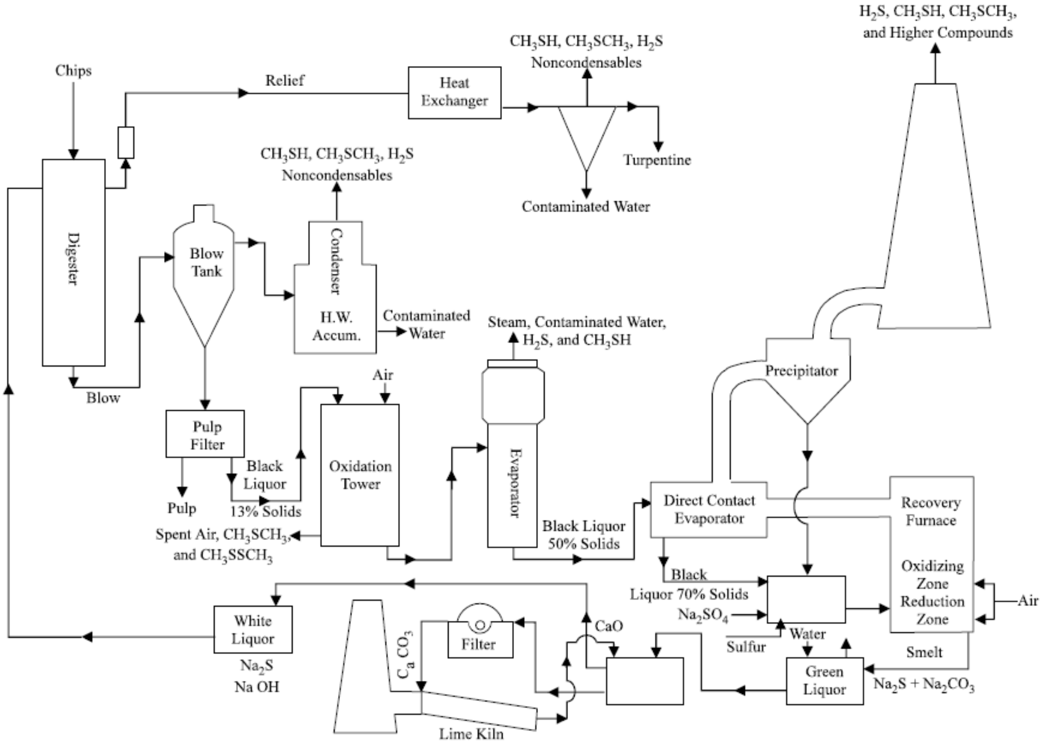


Figure 6 Kraft sulfate pulping and recovery process (Agency & Standards, 1995)

The Kraft process can produce stronger pulp than other pulping processes. A wider range of fiber sources, very resinous types like southern pine and non-wood species like bamboo, can be utilized in the Kraft process. Kraft pulping process can remove most of the lignin present originally in the wood comparing with other processes.

2.2.3 Acid Sulfite Pulping

Acid sulfite pulping process is similar to Kraft process, except cooking chemicals liquor. Sulfurous acid is used to dissolve the lignin in the wood, replacing the caustic solution in Kraft process. However, acid sulfite process provides more degradation of cellulose crystalize leading to weaker fibers. A bisulfite of sodium, magnesium, calcium, or ammonium must be used for buffering the cooking solution.

Digestion is performed in the presence of a sulfurous acid/bisulfite cooking liquid at high pressure and temperature, in either batch or continuous digesters. Red liquor, the spent sulfite liquor, is drained through the bottom of the tank and then sent to a recovery plant to recover heat and chemicals, treated and discarded, or incinerated. The pulp is then washed and then screened and centrifuged to remove knots, bundles of fibers, and other material. It subsequently may be bleached, before being pressed and dried in papermaking operations.

Because of the variety of cooking liquor bases used, numerous ways evolving for heat and/or chemical recovery based on type of cooking liquor base. Calcium based systems that chemical recovery is not practical, and the spent liquor is discharged or incinerated as found mostly in old mills. Ammonium based system can generate heat can by combusting the spent liquor, but the ammonium base is not thereby recovered. In sodium or magnesium based systems, both of sulfur and base, and heat may be recovered.

In heat recovery process, weak red liquor is concentrated to 55% solids in a multiple-effect evaporator and then 55 to 60% solids by direct contact evaporator. This concentrated liquor is sprayed and burned into a furnace for steam production. The steam is used for operating the digesters, evaporators, etc. and to meet other power requirements.

Cooking chemical recovery is performed in magnesium base system. Magnesium base liquor is burned to form magnesium oxide as fine white power in a multiple cyclone. A flue gas also is produced from burning magnesium base liquor. The magnesium oxide is then slaked with water to form circulating liquor in a series of venturi scrubbers. Magnesium oxide as circulating liquor is used to absorb sulfur dioxide from the flue gas in a series of venturi scrubbers providing a bisulfite solution for cooking process. In sodium based system, the spent sodium based liquor is burned to recover the inorganic compounds as a molten smelt containing sodium sulfide and sodium carbonate. This smelt may be processed further to absorb sulfur dioxide from the flue gas. However, the smelt may be sold to a nearby Kraft mill as raw material for green liquor production.

If liquor recovery is not practiced, an acid plant is necessary of sufficient capacity to fulfill the mill's total sulfite requirement. Normally, sulfur is burned in a rotary or spray burner to produce gas that is then cooled to apply heat by heat exchangers. The cooled gas is then absorbed in either limestone or a solution of the base chemical. This process is similar to practiced liquor recovery, although a much smaller amount of sulfur dioxide must be produced to make up for that lost in the process.

2.2.4 Neutral Sulfite Semichemical (NSSC) Pulping

In this method, wood chips are cooked with a neutral solution of sodium sulfite and sodium carbonate. The role of Sulfite ions is to attack the lignin in wood whereas the sodium bicarbonate acts as a buffer to maintain a neutral solution. Only a portion of the lignin is removed during the cook, after which the pulp is further reduced by mechanical disintegration in contrast to Kraft and acid sulfite processes. This method achieves yields as high as 60 to 80%, as opposed to 50 to 55% for other chemical processes. The NSSC process varies from mill to mill. Some mills dispose of their spent liquor or recover the cooking chemicals. Some mills are operated in combination with Kraft mills, by mixing their spent liquor with the Kraft liquor as a source of makeup chemicals.

2.3 Integrated Biorefinery Options with pulping process

Biorefinery process options has been studied to transform pulp and paper mill into Integrated Forest Biorefinery involving hemicellulose pre-extraction, black liquor gasification and removal of lignin from black liquor. Hemicellulose pre-extraction and lignin precipitation are biochemical technology, but black liquor gasification is thermochemical. The choice of implemented biorefinery technologies depend on the set of marketable products that are expected in the supply chain. The impact on pulp production, capital and operating cost will vary with the choice of implemented technologies.

2.3.1 Pre-extraction of Hemicellulose

In hardwoods, hemicellulose composes the O-acetyl-4-O-methylglucuronoxylan, whereas the O-acetylgalactoglucomannan is the predominant component in the softwood. Sugars composed in hemicellulose are hexoses including glucose, mannose and galactose, and pentoses including xylose and arabinose. Hemicellulose can be extracted via pretreatment processes to be used as raw material for biochemical production. Pretreatment methods for hemicellulose hydrolysis and fractionation have been studied in detail (Bajpai, 2013; Raimo, 2015).

- Dilute acid
- Liquid hot water extraction
- Dilute acid-steam explosion
- Alkaline extraction
- Ammonia fiber/freeze explosion (AFEX)
- Organosolv fractionation
- Supercritical carbon dioxide

- Ionic liquids (new class of solvents with non-molecular, ionic character that are liquids at room temperature)

The transformation of a Kraft pulp mill into an Integrated Forest Biorefinery requires the Pre-extraction of hemicellulose for implementing biorefinery unit instead of typically steam production by burning in the recovery boilers. Pre-extraction of hemicellulose provides a new feedstock for value added biofuel and biochemical production that can generate new revenue stream for the pulp and paper industry (Ragauskas et al., 2006; Raimo, 2015). A challenge of the pre-extraction process for development is to solubilize hemicellulose sugars with minimal formation of fermentation inhibitors and maximal the fiber integrity. Pre-extraction of these hemicelluloses prior to Kraft pulping is expected as one pathway for integrating biorefinery unit with pulp and paper industry. The benefits of hemicellulose pre-extraction are:

- Reduction in Kraft cooking times.
- Enhancing Kraft cooking liquor impregnation.
- Improved pulp properties.
- Improving pulp production capacity for Kraft pulp mills that are recovery-furnace limited.

These benefits strongly push the implementation of wood hemicellulose pre-extraction technologies in pulp and paper mills (Bajpai, 2013).

For the development of wood chips pre-extraction implementation with existing pulping operations, it is important that quality of pulps that is mainly the strength of the final paper sheet must not be dropped. The strength of the paper sheet will drop if degree of polymerization (DP) of cellulose is decreased beyond its normal (Yanagisawa et al., 2005). It is the fact that cellulose is the primary element in a lignocellulosic complex, so cellulose properties directly relate to the fiber strength implicating paper strength. Therefore, the employment of any hemicellulose pre-extraction technology in pulping process should be minimized the hydrolysis of cellulose to keep quality of pulps. Hemicellulose plays role as adhesive in fiber relating to increasing strength of paper. Kraft pulps consisting of higher than ~80% of α-cellulose lead to lower strength of paper sheet (Bajpai,2013). Hence, the limit of extracted hemicellulose also depends on pulping product specification. It was reported that it is possible to keep the same productivity, yield and quality of pulp when hemicellulose is pre-extracted under 15-20%. However, black liquor solids load feeding to the recovery boiler for steam production will be decreased.

2.3.2 Black Liquor Gasification

Black liquor, residual from delignification step in the pulping process, is a large quantity, approximately half of the wood used in pulp and paper production. To recover cooking inorganic chemicals, organic compound in black liquor is traditionally removed by burning in recovery boiler. Black liquor burning can generate process steam and power for the mill. Black liquor has unique properties that are suitable for gasification (Bajpai, 2013).

Black liquor's properties, which it is liquid and easily pumped into the pressurized gasifier, easy to atomize into fine droplets, highly reactive due to high sodium and potassium content, make the gasification of black liquor easier and more rapid than for any other biomass feedstock.

Black liquor gasification can generate bioenergy that can distribute to biochemical production unit and synthesis gas that can be employed to replace fossil fuels in the lime kiln or used as feedstock for transportation fuel production such as methanol, Fisher-Tropsch liquid, dimethyl ether, hydrocarbon and mixtures of higher alcohols. For this reason, black liquor gasification should be integrated into pulp and paper mill according to an Integrated Forest Biorefinery (IFBR) concept (Bajpai,2013).

Black liquor gasification has been widely interested in biorefining, engineering, pulping, and environmental topics. The key requirement of black liquor gasification is to demonstrate the reliability and feasible of the technology in commercial scale. Several pilot plants have been successfully performed. Integration of gasification process has been emphasized for energy self- sufficiency without fossil fuel usage for pulp and paper mills.

In the gasification process, organic substance in black liquor is partially oxidized with an oxidizing agent to produce syngas replace burning for steam production. The syngas is cleaned to remove contaminated particle, tars and organic species (i.e., alkali vapor species, SO_2, and H_2S). The purpose of syngas cleaning is to prevent the gas turbine damage and reduce pollutant emissions. After cleaning step, syngas is burned to produce electricity by gas turbines together with generators. Next to gas turbine, heat exchanger will apply hot gas from gas turbine for high-pressure steam production. This steam can be used with a steam turbine and/or as process steam. Condensed phase (smelt) continuously leaving the bottom of the gasifier that is digester chemical must be processed further in the lime cycle for chemical regeneration

Essentially, black liquor gasification process causes the alkali species and sulfur species separation that a natural partitioning of sulfur to the gas phase (primarily H_2S) and alkali species to the condensed phase. In the other hand, the typical recovery boiler does not cause this separation that all of the alkali species and sulfur species, mostly as Na_2S and Na_2CO_3, leave in smelt (condense phase). Gasification at high temperatures thermodynamically favors a higher splitting of sodium and sulfur than low temperatures gasification because of higher amounts of sulfur in gas phase. This large amount of sulfur species in gas phase as H_2S may be recovered via absorption to improve pulping chemistries. Numerous patents of industry processes attainably use green or white liquor as an absorbing solvent for this sulfur species absorption (Raimo,2015).

Each mole of sulfur that goes into the gas phase, one more mole of Na_2CO_3 is formed in the condensed phase. The splitting of sodium and sulfur causes a higher amount of Na_2CO_3 in the green liquor because less sulfur in the smelt is available leading to less Na_2S. In lime kiln, the increasing of Na_2CO_3 provides higher causticization loads and increases fossil fuel usage to run the lime kiln unit. For these reasons, higher raw material and operating costs are occurred, so this problem must be eliminated or reduced in order to obtain economic feasible of gasification process.

Before black liquor technology can totally replace the current recovery boiler technology, it is important that this process must be verified that more economically attractive. One topic that requires attention is the causticization process. Gasification technology makes the lime cycle significant increases in capacity contributing to significant increases in fossil fuel consumption, so the development of causticization technologies must be considered to improve economic viability.

Black liquor gasification technologies can be divided into two major classes, low and high temperature gasification (Patrick, 2003). Low-temperature gasification units normally operate at 600-850 °C, below the melting point of inorganics, thus avoiding smelt-water explosions. While, high-temperature gasification units generally operate in the range of 900-1,000 °C, above the melting point of inorganics, leading to melting of smelt. In low-temperature gasification, the alkali salts remain as solid products, while in high-temperature gasification alkali salts is molten. So, fewer constraints for material construction are required due to the solid product in low-temperature gasification. However, the syngas produced from low-temperature gasification may contain larger amounts of tars. These tars can contaminate gas clean-up operations and gas turbines upstream of the gasifier. This problem can cause a loss of fuel product (Schlesinger et al., 2006). Gasification is a well-established technique, but its application to black liquor is new that need to specific research. Several other issues need to be considered.

2.3.3 Removal of Lignin from Black Liquor

When recovery boiler capacity is limit of annual pulp production, it can annually produce extra tons of pulp black liquor by separating lignin from black liquor by precipitation (Lourençon et al., 2015). Lignin is excited as a renewable material for future. From a short-term perspective (0-5 years), lignin is mostly burned as a biofuel for the pulp mill itself and companies that desire to move away from the dependent on fossil fuels. Most of today's market pulp mills are self-sufficient in steam, from the black liquor alone, and have great potential to be energy suppliers to other industries and consumers. The excess energy in mills is exported in different ways, for example, as electricity, biofuels such as bark and lignin, and heat for district heating. However, lignin has potential to generate much more its value in the future. Lignin as biorefinery raw material could be converted to high value-added biochemical replacing petrochemical. Lignin could become material that is globally used in many different applications. Lignin can be used as a high-quality biofuel, raw material for biochemicals and biomaterials production.

"LignoBoost" is possible process to efficiently extract lignin from the black liquor in Kraft mill (Per, 2010). LignoBoost (Figure 7) is supplied by Metso including all the equipment necessary for lignin extraction. There are four main units in the LignoBoost process: precipitation, dewatering, resuspension, and final washing (Tomani, 2010). LignoBoost has been developed through research cooperation between Innventia and Chalmers University of Technology. There are the collaborating of Metso and Innventia for the research and development of LignoBoost and the application of lignin as biofuel. LignoBoost process has been demonstrated as plant in Bäckhammar. This plant achieved the fast production of high-quality lignin at a low cost. Lignin produced directly from the LignoBoost plant has very good properties including 65-70% dry solids content, ash content of 0.1-0.5%, sodium 0.01-0.4%, and heating value of 26 GJ/t. It can be used as biofuel, replacing coal and oil, i.e., in pulp mill's power generation or in lime kilns. In addition, the extracted lignin is also of interest as a raw material for plastics, coal fibers, and chemicals. LignoBoost is looked as a vital process in the development of modern pulp and paper mills with Integrated Forest Biorefinery.

Precipitation step of lignin extraction must use carbon dioxide. Carbon dioxide from the lime kiln could be used but gas cleaning is a challenge. It is possible to apply pure carbon dioxide from ethanol fermentation about one ton of pure carbon dioxide per a ton of produced ethanol. When lignin extraction is combined with ethanol production, the efficiency of carbon dioxide utilization and the economic performance can be improved. The available of extracted lignin and xylan in black liquor depends major on the status of the recovery boiler. In general, the critical level of lignin extraction from black liquor is in a range of 10 to 30 percentage of removed lignin. To compensate for lost heat value, one interesting solution is fuel gas from gasification. Also, carbon dioxide from gasification process can be used for lignin precipitation (Weizhen, 2015).

Lignin as fuel is only the first step of lignin utilization. Lignin can also be converted into a wide range of products. For huge market of plastics industry, lignin could potentially be used as a base chemical substituting petrochemical. Phenols are example biochemicals from lignin that have potential to substitute from petrochemical. Global production of phenols from fossil substance was 8,000,000 tons in 2006 (Bajpai, 2013). Moreover, lignin can also be converted into a renewable fuel. In the future, lignin has potential as a base substance that is used with a wide range of applications and a global market. So, lignin extraction that is combined with pulping process could improve pulp and paper industry in term of economic and environmental issues.

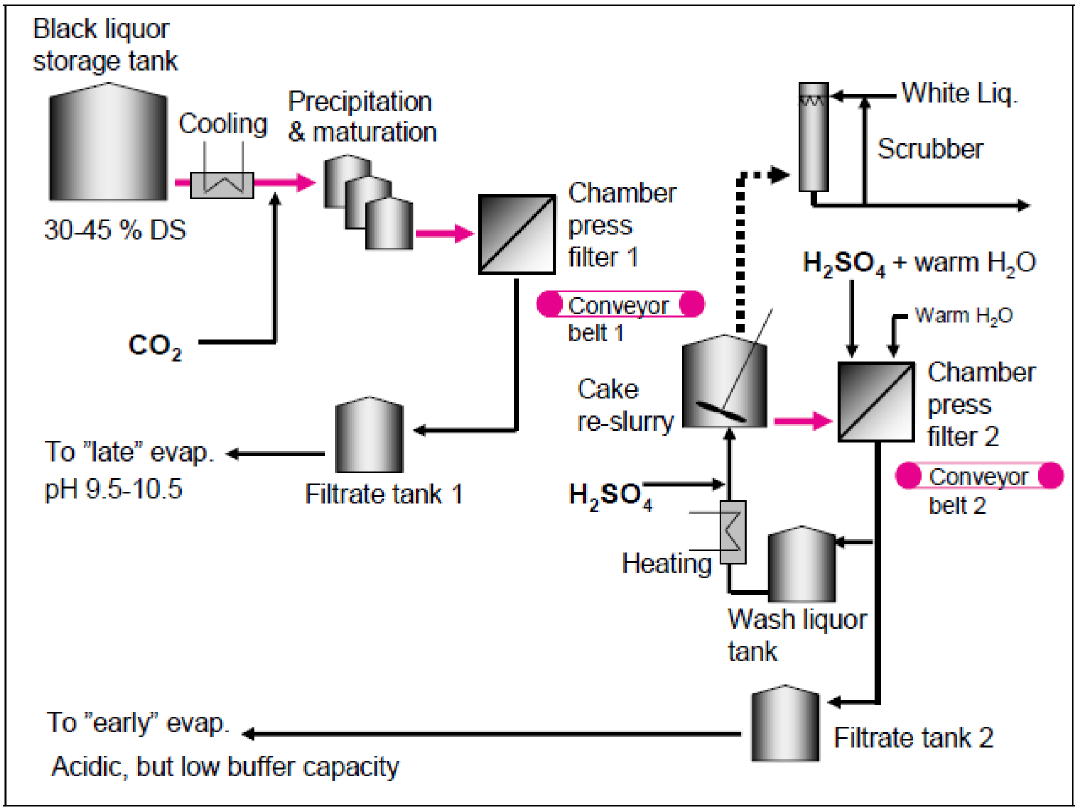


Figure 7 LignoBoost process (Per, 2010)

2.4 Integrated Forest Biorefinery Implementation Strategy

The integrated forest biorefinery has been seriously considered by pulp and paper industry as a strategy for transforming their basic business model into new more sustainable model with optimizing the value of existing assets and pursuing new product development. The strategy which can improve the pulp and paper industry together with risk minimization is challenged. The selection of the integrated biorefinery products and technologies must have a promising market potential over the long-term. Integrating of biorefinery platform should also consider the changes of existing process such as process risks related with added innovative processes, increased process complexity with new product manufacturing, yields and overall mass/energy balances, process constraints related to supply chain flexibility, and co-product opportunities. The understanding of an existing supply chain is vital knowledge to specific supply chain opportunity of the industry. Integrated forest biorefinery design is complicated problem that must solve by a multidimensional and multidisciplinary approach, including customer/product and process concepts in order to not only a capital project, but achieve also the business transformation.

The strategic changes of whole business refer to Enterprise Transformation (ET). ET implies evolving aggressive corporate-wide initiatives to impact the strategies, structures and human system of the corporation—as well as to create more sustainable and profitable organizations (Mansoornejad et al., 2010). DuPont is one of the most successful examples of the business transformation by adapting core business to market needs, Figure 8.

Chambost and colleagues (Chambost et al., 2008) referred to Enterprise Transformation applying with integrated forest biorefinery implementation. They said that “pulp and paper industry is to achieve the implementing forest biorefinery when ET must be performed in two broad ways: “inside-out” and “outside-in”. “Inside-out” Enterprise Transformation relates to transforming the enterprise in terms of processes and manufacturing culture, but the current mission/vision of the company is kept unchanged. In the other hand, “Outside-in” Enterprise Transformation is the change in core mission/vision as well as products delivered to the marketplace in order to meet current market demand. These concepts are familiarly linked to the transformation of the pulp and paper industry that have been assembled into a phased approach: phase I projects lower operating costs, phase II projects increase revenues, and phase III projects optimize margins.

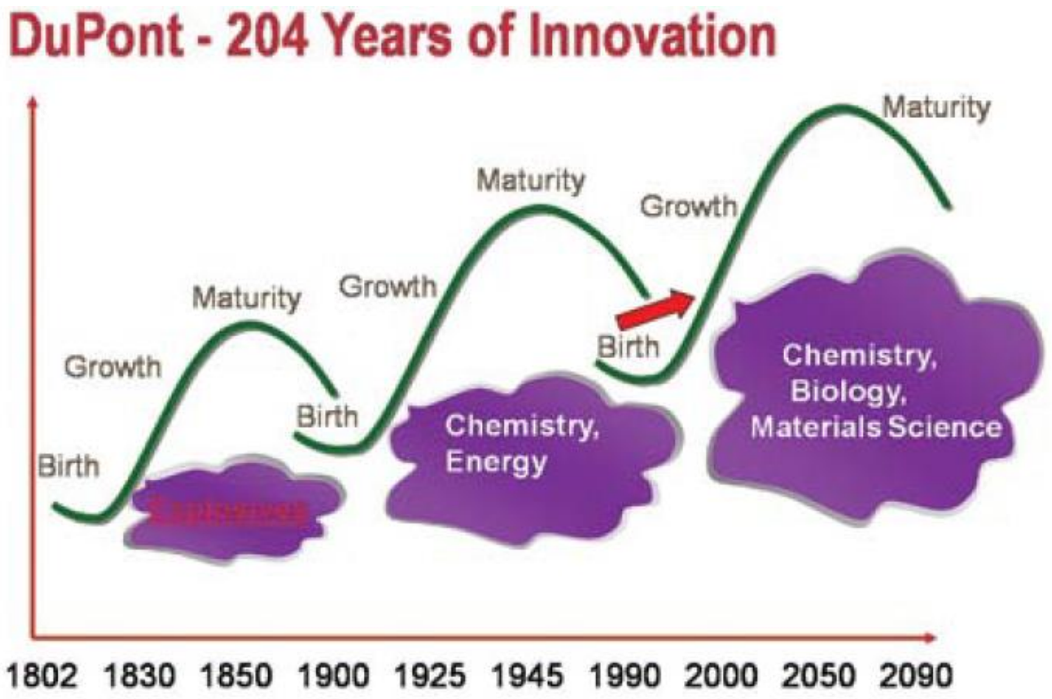


Figure 8 Example of Enterprise Transformation of DuPont (Chambost et al., 2008)

Phase I have not any change in the core business. Objective of phase I is to reduce operating costs by implementing biofuel production substituting fossil fuels usage, or seeking new alternative feedstocks apart from woody biomass, such as agricultural wastes or local industry waste. The company’s competitive strengths involving know-how about responsible and effective harvesting, and existing infrastructure are dragged to generate new biomass harvesting techniques, bioenergy technologies and the potential for carbon credits. Since company’s capital spending budget is limited, phase I projects would compete for capital. Cost reduction, technology development support and carbon credits are seriously considered to minimize risk and improve productivity.

Phase II relate to an “outside-in” transformation. The core mission and vision of company must be changed together with the product mix distributed to the market to enlarge the product portfolio. Value-added products would be generated through biorefinery technology as the potential of a significant revenue diversification for the company. Thereby, the most sustainable product/process portfolio is judiciously selected to increase revenue for company.

Phase III comprises an “inside-out” transformation that transforms work and process steps for the new product mix. Phase III involve optimizing margins by play on manufacturing flexibility through “knowledge-based manufacturing” to seek improved bottom-line results. Knowledge-based manufacturing involves using detailed knowledge of process capability for flexible production, and advanced supply chain optimization techniques for product planning over different time horizons and identifies the trade-offs between product orders, anticipated supply and demand and manufacturing flexibility. Successful of Phase III contribute to improvements in free cash flow, ability to handle price volatility and sustainability for the longer term It is important that the companies must design completely all three phases before In order to succeed, companies must design all three phases of the biorefinery before perform phase I projects. Summary of the 3-phased approach is illustrated by Figure 9.

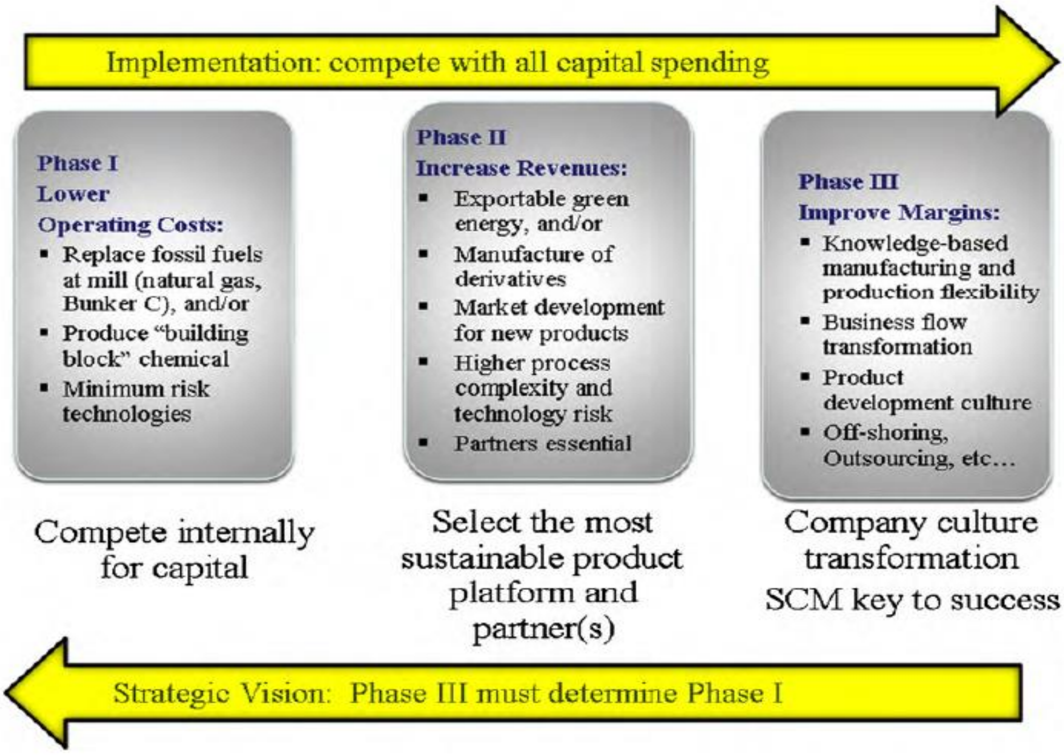


Figure 9 Phased approach of the strategic implementation of biorefinery (Chambost et al., 2008)

According to the phased approach of Enterprise Transformation concept, Mansoornejad et al. (2010) proposed three steps hierarchical methodology involves product/process portfolio design, design of manufacturing flexibility, and supply chain network design. First, the promising product/process portfolio, that involve product to be produced and process to be employed, must be defined. First step is divided into two sequential parts including product portfolio definition and large block analysis for generation of product/process portfolios to screen out non-profitable portfolios. In second step, each process is determined the range of production rate as design target and the production lines is designed to determine best design alternative that can represent the targeted flexibility. Final step is supply chain network design for each product/process portfolio. Supply chain network alternatives will be generated for each portfolio. Each supply chain network alternative is determined its supply chain profit. The best supply chain network alternative can then be determined for each portfolio. Figure 10 provides the step by step overview of this hierarchical methodology. A set of feasible and practical biorefinery options, not the best one, which a company can strategically pursued is seek by this methodology.

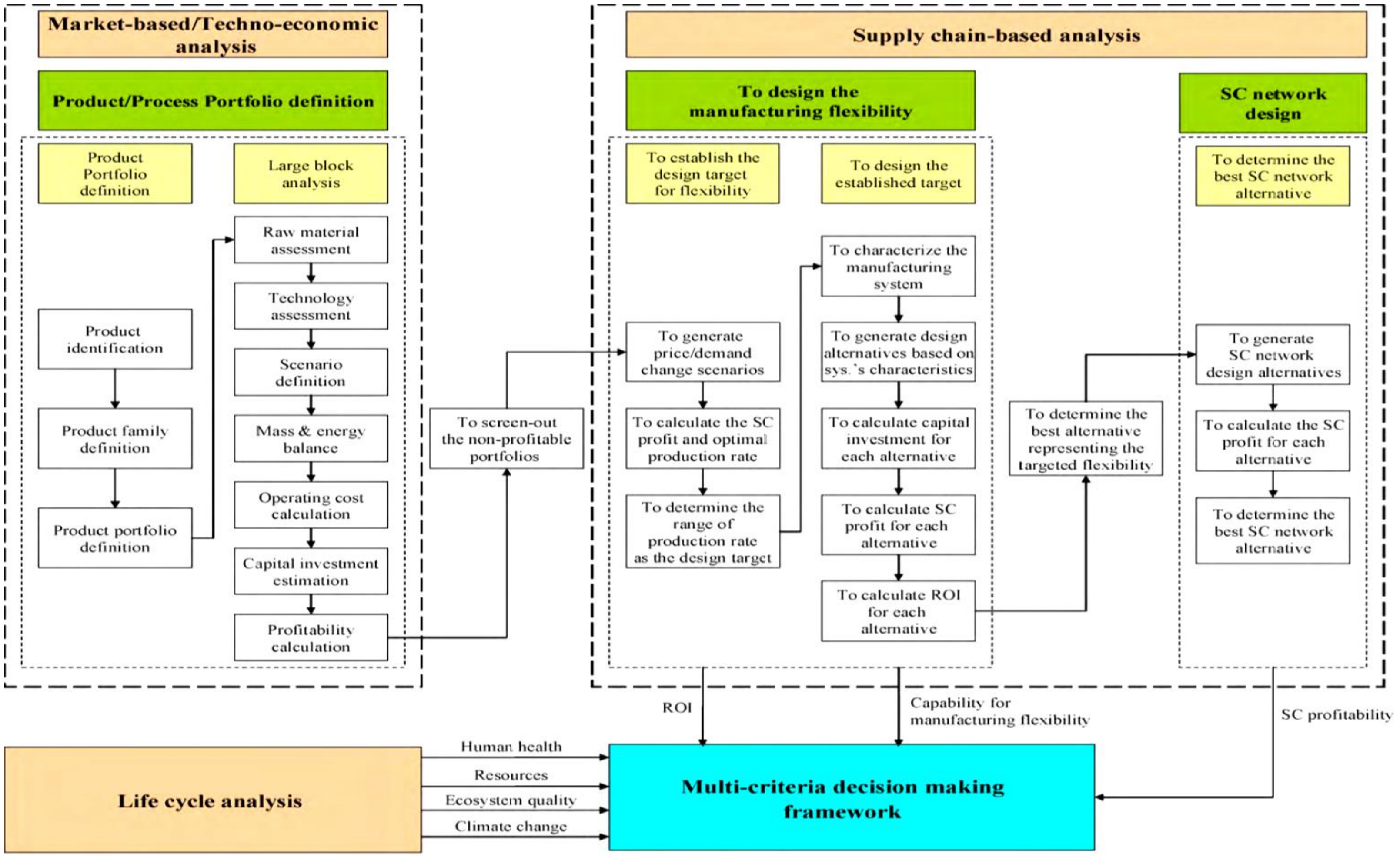


Figure 10 The hierarchical methodology (Mansoornejad et al., 2010)

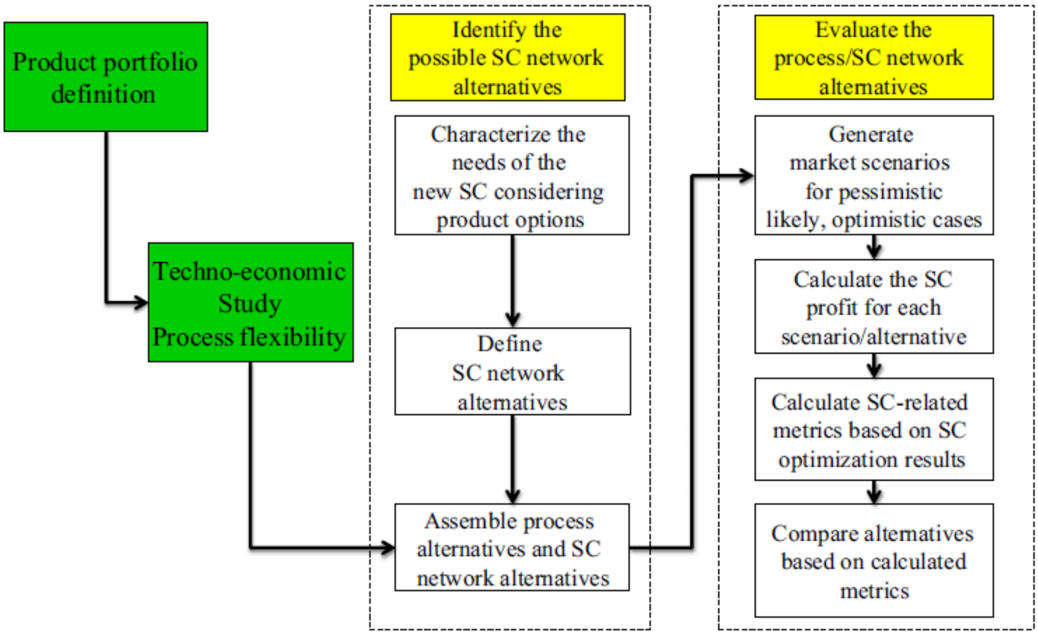
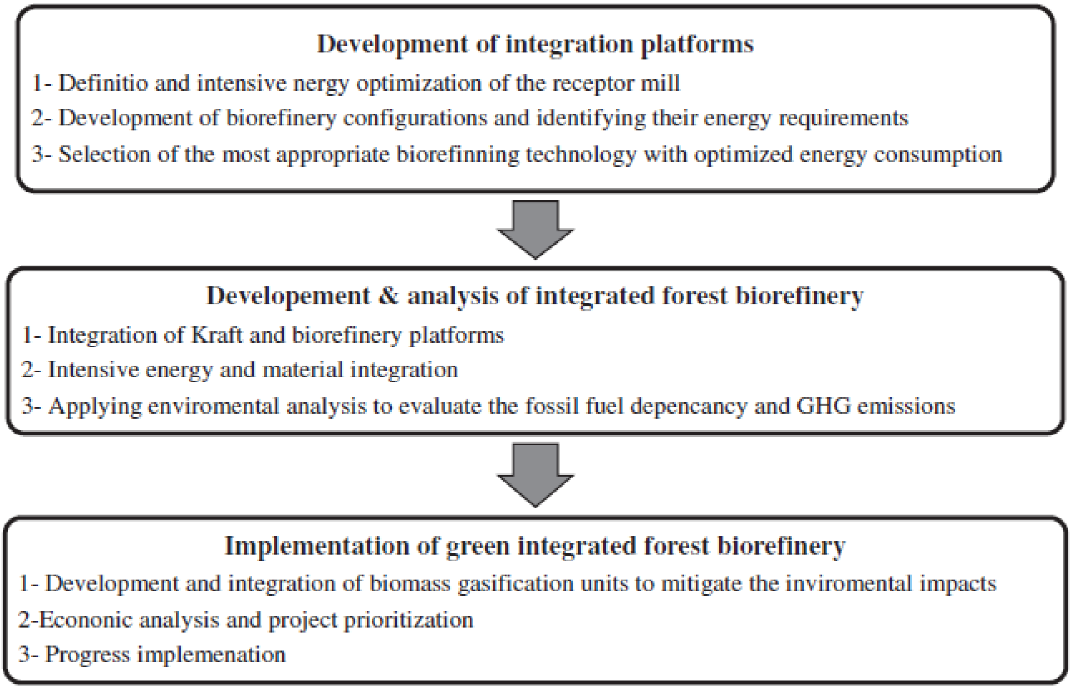


Figure 11 Scenario-based methodology for the supply chain network design (Mansoornejad et al., 2013)

Then in 2013, Mansoornejad and colleagues (Mansoornejad et al., 2013) further introduced a scenario-based approach to strategically design and analyze supply chain for forest biorefinery based on the impacts of the design on operational supply chain activities. They said that instead of using large-scale supply chain mathematical formulations which consider thousands of options, a practical scenario-based approach can be used to identify the possible options and evaluate their performance in the long-term operation. Biorefinery alternatives involving product portfolio, process alternatives and supply chain network configurations can be evaluated using this scenario-based methodology proposed. The step wise methodology is employed to consider the practical aspects of design into decision making by demonstrating the impact of each scenario on supply chain profitability. Step by step workflow for scenario-based approach is showed in Figure 11. From Mansoornejad's work (Mansoornejad et al, 2010), the output of product portfolio definition methodology is a set of product/process portfolios that will be used as input to the scenario-based methodology comprising of two parts. First, possible supply chain network alternatives are identified and after that combined with product/ process portfolios, in the second part, product/process/supply chain network alternatives are evaluated based on their performance at each generated market scenario. By comparing the profitability of alternatives as well as their robustness in volatile market conditions, a set of biorefinery alternatives to be considered can be identified.

Meanwhile, the concept of green integrated forest biorefinery with Kraft process and the strategy for its progressive implementation (Figure 12) was introduced by Maryam et al. (2013). They briefly surveyed energy implication of major biorefinery technologies. When lignin or hemicelluloses are extracted from the Kraft pulp line, the heat production capacity from burning black liquor in recovery boiler where is deceased. While the steam demand increases due to the operation of integrated biorefinery unit. In order to avoid fossil fuel consumption, the energy in total site must be intensively integrated and optimized. They proposed that a combination site including specialty wood pulp and bio-product, biomass gasification, power cogeneration and optimal absorption heat cycles for heat upgrading is economical feasible. Because of overall interaction between integrated biorefinery units and a Kraft mill receptor, it is important that intensive energy and material integration must be performed. To eliminate fossil fuel consumption and supplement steam production, gasification units should be implemented into Green Integrated Forest Biorefinery. They said that the successful implementation of intensive energy integration and optimization measures lead to sustainability of Integrated Forest Biorefinery implementation.

In 2014, the Green Integrated Forest Biorefinery (GIFBR) with zero fossil fuel usage was proposed by Rafione et al. (2014). They also proposed a methodology to develop a GIFBR based on an existing Canadian Kraft pulping mill. Their research aim is zero fossil fuel consumption that is of particular interest from and environmental and economic point of view, but the development of such a facility is complex. An overview of this GIFBR concept is presented on Figure 13. A progressive implementation strategy is recommended, and it involves five different phases, as illustrated on Figure 14.



Development of integration platforms

1- Definitio and intensive nergy optimization of the receptor mill
2- Development of biorefinery configurations and identifying their energy requirements
3- Selection of the most appropriate biorefinning technology with optimized energy consumption

Developement & analysis of integrated forest biorefinery

1- Integration of Kraft and biorefinery platforms
2- Intensive energy and material integration
3- Applying enviromental analysis to evaluate the fossil fuel depencancy and GHG emissions

Implementation of green integrated forest biorefinery

1- Development and integration of biomass gasification units to mitigate the inviromental impacts
2-Econonic analysis and project prioritization
3- Progress implemenation

Figure 12 Progressive implementation of Green Integrated Forest Biorefinery (Maryam et al., 2013)

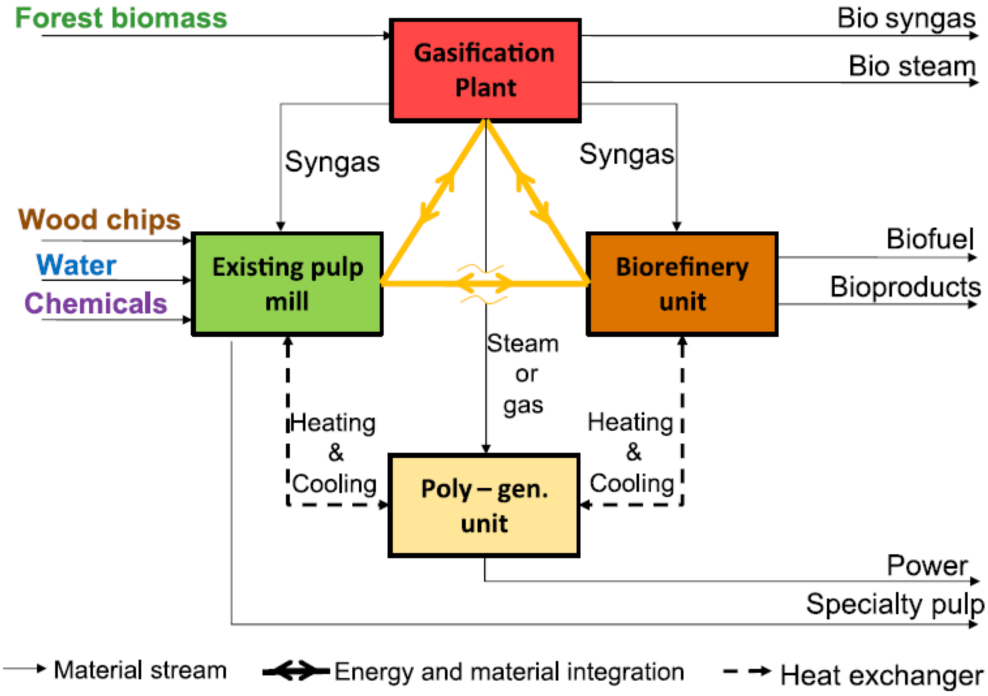


Figure 13 Overview of the Green Integrated Forest Biorefinery concept (Rafione et al., 2014)

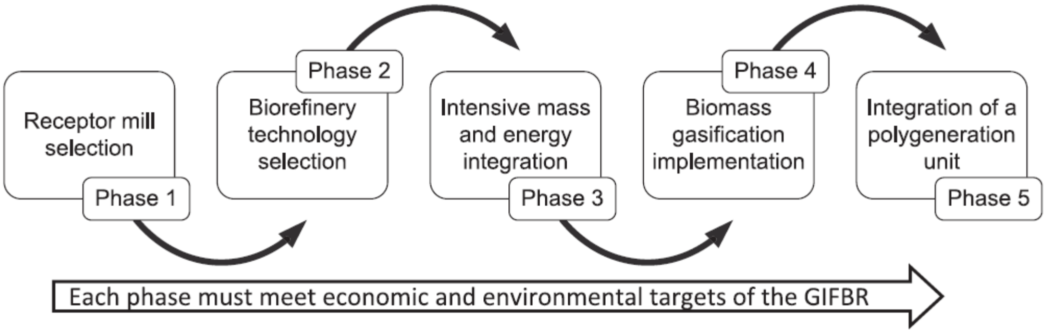


Figure 14 Methodology for the development of a GIFBR (Rafione et al., 2014)

2.5 Systematic framework for development of biorefinery-integrated system

There are various concepts in the field of biorefinery technologies and diverse technical research in biofuel and biochemical productions (Brodin et al., 2017; Kajaste, 2014)). Such varieties lead to a largely complex network of alternatives such that the appropriate processing pathways are difficult to select. Accordingly, technologies for realistic productions of high-value products derived from reasonable raw material should be systematically determined (Hämäläinen et al., 2011).

Several biorefinery-related studies adopted the systematic framework with the assistance of mathematical programming for process synthesis and design such as the production of thermochemical bio-fuels (Gassner & Maréchal, 2009), the NREL bioethanol production (Alvarado-Morales et al., 2009), the multi-product biorefinery system with petroleum-based gasoline (Zondervan et al.,2011), the biodiesel production from microalgae (Rizwan et al., 2015), the chemical synthesis via CO_2 utilization (Kongpanna et al., 2016), the multi-product wood-biorefinery production (Schroder et al., 2019) and recently the design of multiproduct biorefinery for succinic acid, acetic acid and DME productions using pulp logs (Ghayur et al., 2019).

Generic framework proposed by Quaglia et al., 2012 was developed for the synthesis of a processing network (or the superstructure modelling) contained subparts of processing intervals. A large amount of data associated with each processing interval such as information of mass and energy balances were compiled from diverse sources. After the superstructure generation and optimization was carried out, the optimal pathway of the processing network was to be determined; called the synthesis-design problem. Since this problem was categorized as a decision-making type (i.e. which route is optimal?), the superstructure was transformed into mathematical models that contained decision variables for optimization. Mixed-integer nonlinear programming (MINLP) was used in order to obtain the optimal network topology.

2.5.1 Process synthesis

Process synthesis is to synthesize the optimal process based on the defined objective. The synthesis problem includes a set of different raw materials, products and processing pathways including sequence and equipment to get the optimal configuration. The methods such as heuristic, mathematical programming, and hybrid methods would be performed to address the problems.

2.5.2 Heuristic

Heuristic methods implement a set of rules based on collected know-how and expert knowledge to solve problem in a systematic manner. Though it is beneficial in term of ease of use and fast solutions, the solution is based on available knowledge leading to all the alternatives are not considered and the global optimization cannot be promised. the rules can also be inconsistent with some problems. The heuristics of entire chemical processes are limited.

The hierarchical approach first introduced by Douglas (1985) decomposes the problem into various levels in order called a hierarchy of decisions. There are five levels: (i) batch vs continuous, (ii) input-output structure, (iii) recycle structure and reactor considerations, (iv) separation system specification (vapor recovery or liquid recovery), and (v) heat exchanger network. This is the foundation of further heuristic methods for synthesis of entire chemical processes.

The synthesis methods integrated thermodynamic laws and properties are implemented to analyze aspects of the synthesis. For synthesis of separation systems, Jaksland et al. (1995) exploit the different physical properties related to different separation processes. This work was adapted for entire processes by Jaksland and Gani (1996). This method incorporates thermodynamic-based algorithms and implement necessary data and tools to basically understand the system and thereby design the process. Graphical techniques representing the thermodynamic behavior could be applied. For this method, the process sequences are formulated based on properties indicative of certain behavior and then combined using combinatorial laws similar to the computer aided molecular design (CAMD) problem.

2.5.3 Mathematical programming

Process synthesis problems can be also formulated and solve via the mathematical optimization. However, it has limitation for global optimality due to their size (computationally intensive) and complexity. A superstructure optimization approach for process flowsheet synthesis was mentioned in Grossmann (1990). A superstructure illustrating the network of alternative processing units and their possible pathway was modeled by discrete or binary variables to make decision based on the information of alternative units and optimizing objective. To define optimal configuration based on the superstructure formulation, optimization techniques and solution strategies are required to solve superstructure optimization problem as Mixed Integer Non-linear Programming (MINLP).

Once, MINLP solution strategies was proposed by Duran and Grossmann (1986) with an Outer-Approximation (OA) algorithm which was further improved (Kocis and Grossmann, 1987, 1989; Turkay and Grossmann, 1998). The OA algorithm was divided into two parts. First, Non-linear Programming (NLP) sub-problem with the initial continuous variables are optimized for a specific flowsheet structure. Second, the Mixed Integer Linear programming (MILP) master problem are also optimized for obtaining an optimal configuration. However, this approach limits for non-convex problems. Thus, the Generalized Disjunctive Programming (GDP) was developed to alternatively represent mixed integer programming (Raman & Grossmann, 1994). Moreover, the Modeling/Decomposition (M/D) strategy for solving the Outer Approximation with the Equality Relaxation (OA/ER) algorithm was applied and proposed by Kocis and

Grossmann (1987 & 1989), which the superstructure was separated into nodes (process units) and their interconnections. An extensive review on MILP and MINLP techniques provided by Grossmann (2002).

Recently, Quaglia et al. (2012) proposed a process synthesis framework with integrating business and engineering aspects. This framework involves a generic process interval model representing the processing units to formulate the different alternatives into the same model. This generic process interval model was modified from superstructure model with biorefinery network proposed by Zondervan et al. (2011). The unique methods and tools were required for the proposed framework to formulate the model as MINLP. There are various case studies which applied this method for process synthesis including the synthesis of chemical processes (Lee and Grossmann, 2003) bio-refinery processes (Martín &Grossmann, 2013), wastewater treatment networks (Quaglia et al., 2014).

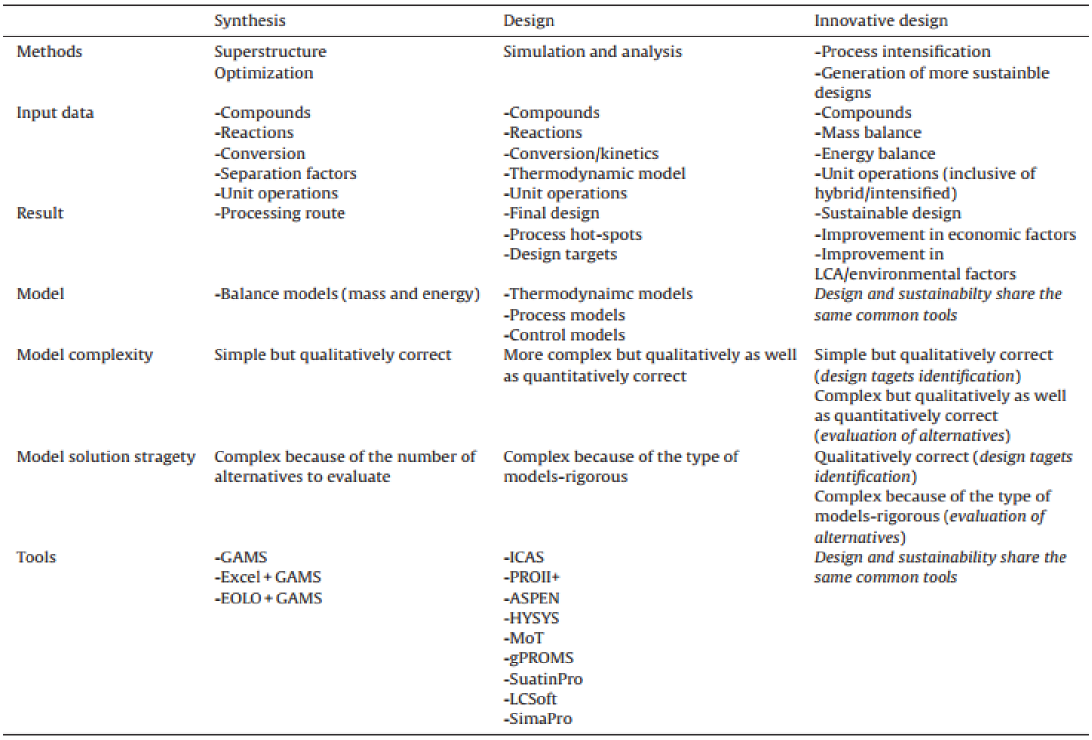
2.5.4 Hybrid

Both heuristic and mathematical programming approaches have their own advantages and disadvantages. So, the hybrid methods aim to deliver their advantages and avoid some disadvantages that concentrate on the narrow search space to lessen the size of the synthesis problem and define near-optimal solutions which forward to process analysis in more detail.

A framework using hierarchical decomposition and mathematical optimization methods was proposed to generate and screen process alternative by Mészáros & Fonyó (1986) and Mizsey and Fonyo (1990). Also, Hostrup et al. (2001) modified thermodynamic insights and mathematical programming involving three main steps. (i) pre-analysis, (ii) flowsheet and superstructure generation using thermodynamic insights, and (iii) simulation and optimization when MINLP models are formulated and solved. d'Anterroches and Gani (2005) presented a framework for computer aided flowsheet design (CAFD) for flowsheet synthesis in the same way of molecular formation by atoms or groups in computer aided molecular design (CAMD) techniques. This framework adapted for different flowsheet property models are successfully applied to biochemical processes (Alvarado-Morales et al., 2010).

Babi et al, 2015 introduced 3-stage frameworks which was employed in this work, intensively describe in Chapter 4. For process synthesis–intensification methodology, the integrated task-phenomena based approach was implemented to perform a multi-scale synthesis for alternative generation after synthesis and base case design by heuristic and/or mathematical programming methods. There are two main tasks. First, the unit operations scale was decomposed into the task scale (Siirola, 1996) and phenomena scale (Lutze et al., 2013; Babi et al., 2014), then phenomena are combined (rule-based) in such a manner of performed task or a set of tasks. These combinations of phenomena and/or tasks were converted into unit operations based on technical knowledges. Consequently, alternatives were acquired to compare to base case for the best sustainable process. Table 3 gives a list of different methods and tools in the process synthesis–intensification framework have been available.

Table 3 Summary information for process synthesis–intensification framework in each stage of work (Babi et al., 2015)



	Synthesis	Design	Innovative design
Methods	Superstructure Optimization	Simulation and analysis	-Process intensification -Generation of more sustainble designs
Input data	-Compounds -Reactions -Conversion -Separation factors -Unit operations	-Compounds -Reactions -Conversion/kinetics -Thermodynamic model -Unit operations	-Compounds -Mass balance -Energy balance -Unit operations (inclusive of hybrid/intensified)
Result	-Processing route	-Final design -Process hot-spots -Design targets	-Sustainable design -Improvement in economic factors -Improvement in LCA/environmental factors
Model	-Balance models (mass and energy)	-Thermodynaimc models -Process models -Control models	*Design and sustainabilty share the same common tools*
Model complexity	Simple but qualitatively correct	More complex but qualitatively as well as quantitatively correct	Simple but qualitatively correct (*design tagets identification*) Complex but qualitatively as well as quantitatively correct (*evaluation of alternatives*)
Model solution stragety	Complex because of the number of alternatives to evaluate	Complex because of the type of models-rigorous	Qualitatively correct (*design tagets identification*) Complex because of the type of models-rigorous (*evaluation of alternatives*)
Tools	-GAMS -Excel + GAMS -EOLO + GAMS	-ICAS -PROII+ -ASPEN -HYSYS -MoT -gPROMS -SuatinPro -LCSoft -SimaPro	*Design and sustainability share the same common tools*

CHAPTER 3

METHODOLOGY FOR PROCESS SYNTHESIS AND DESIGN

Generic frameworks integrating business and engineering assessment for synthesis of processing networks are developed as integrated synthesis methods and tools for superstructure model based on processing intervals (Quaglia et al., 2012). A large amount of data collected from many sources needs to be generated and evaluated for all possible alternatives before the set of mathematical models representing superstructure of the alternatives is solved by supporting tools. The synthesis-design problem is formulated as decision-making model of a superstructure in form of mixed-integer nonlinear programming (MINLP) problem to obtain the optimal network topology. The framework involves mathematical model, an innovated data structure with its databases, and in-house software for a user-friendly interface named Super-O further introduced by Bertran et al. (2016).

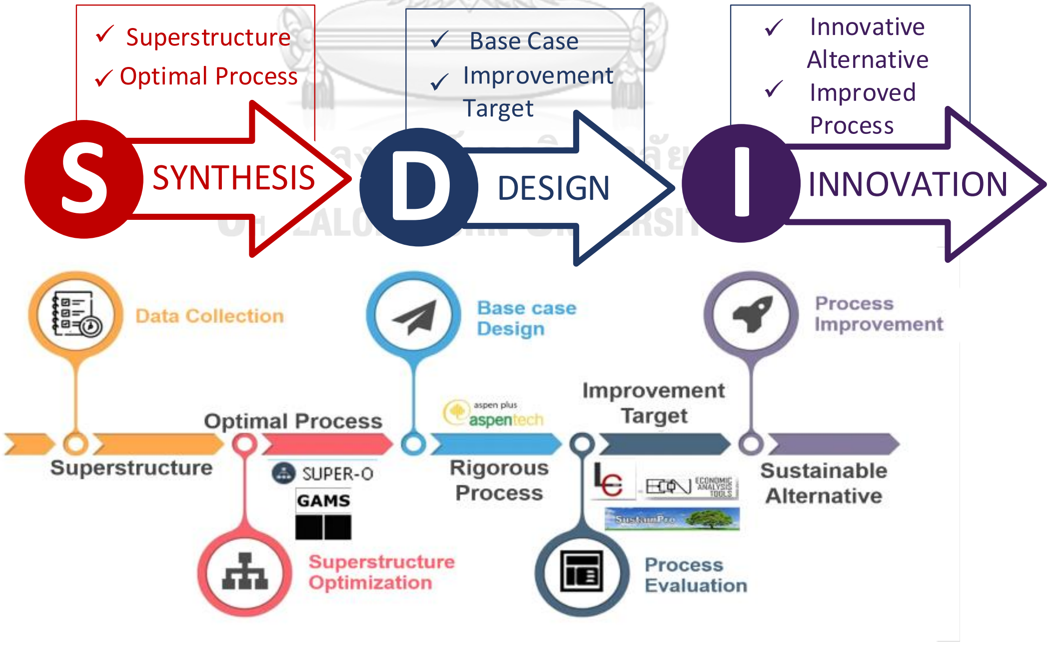


Figure 15 Overview of systematic three-stage framework

As illustrated in Figure 15, a 3-stage approach for sustainable synthesis-design are applied at process synthesis and development of novel integrated biorefinery networks following the framework proposed by Babi et al., 2015. The systematic framework was decomposed hierarchically into three stages: Synthesis (Stage I), Design (Stage II) and Innovation (Stage III). This framework was employed step by step. The output from each stage was transferred to the next stage to achieve the associated objective resulting in a more sustainable biorefinery process. In synthesis stage (Stage I), among numerous alternatives process synthesis was performed to define optimal biorefinery technologies integrated into chemical pulping process subject to specified performance criteria. The optimal process will be considered as a base case for process design (Stage II) performed by process simulation and sustainability evaluation including economics, energy and environmental assessment referred to LCA factors (Kalakul et al., 2014; Khoo et al., 2019). Based on process evaluation, bottleneck for further improvements are defined. The innovative alternative achieving the improvement target is generated and evaluated in innovation stage (Stage III). The workflow is step-by-step described in this chapter as shown in Figure 16.

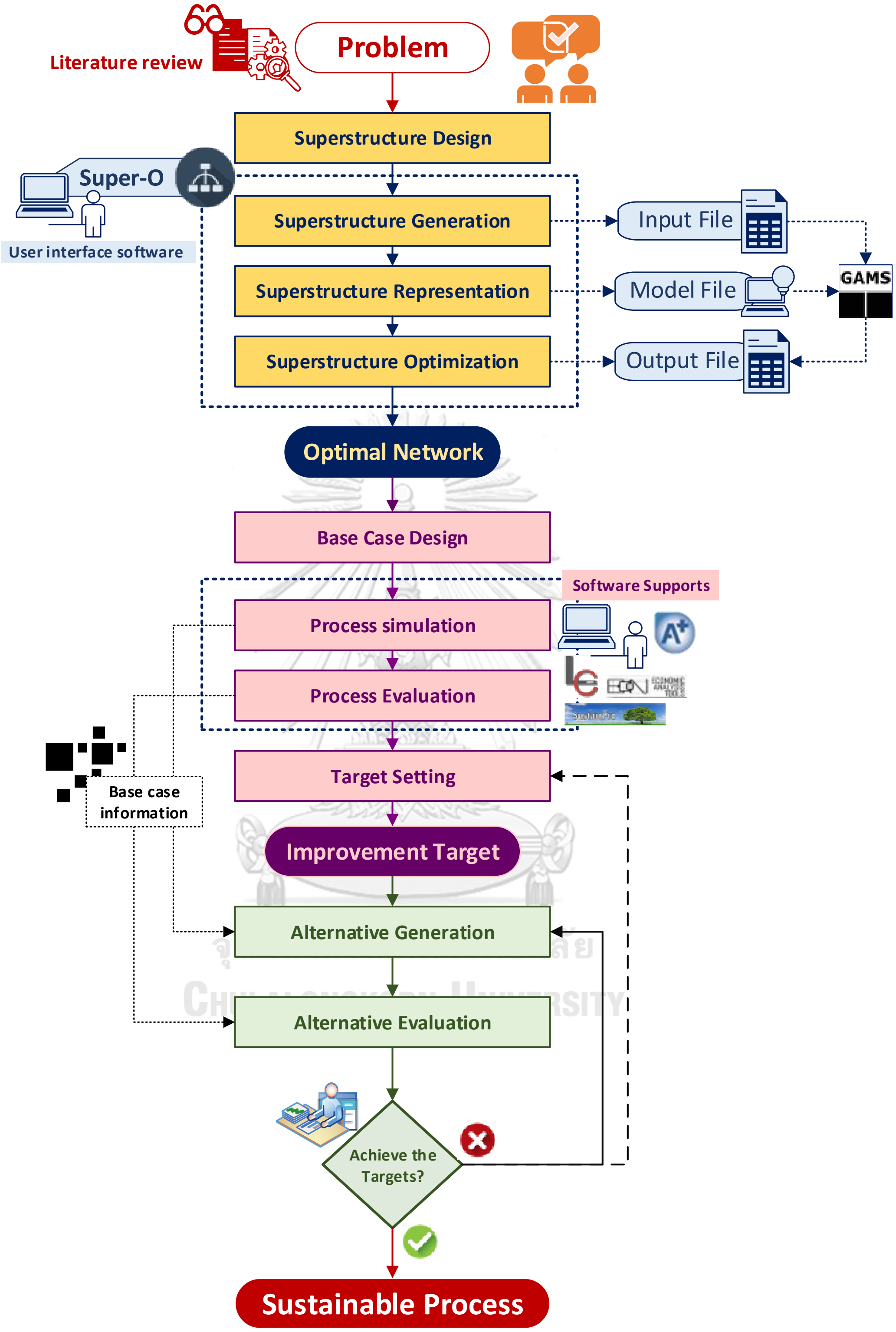


Figure 16 Methodology framework

3.1Stage I: Synthesis

Objective of stage I:	Process synthesis based on problem definition
Method:	Optimization of designed superstructure
Outputs:	Overview of available technologies Database updating Optimal network from superstructure optimization
Support software:	Super-O (In-house interface software), GAMS (Problem solver) and Excel (Storage input/output files data)
Concept:	Process synthesis using superstructure optimization is an effective approach of an integrated business and engineering framework to define the best chemical and biochemical process based on specified process performance and constraint. The scope of process development is established via literature review in this stage. Superstructure is alternatives network of known possible technologies from a literature survey. The associated data of considered technologies is collected to generate the superstructure. The optimal processing network of Integrated Biorefinery System for Thailand will be defined by superstructure optimization. The mathematical problem is determined as an objective function, maximum profit, subjecting to the process constraints and performance criteria. The optimal feedstock, product and processing route is obtained as the promising process, which is defined from designed network of alternative based on problem statement, to further design and

develop in the next stages. The complex of process synthesis problem using mathematical programming needs support by systematic data management and computer-aided tools for solution. As shown in Figure 16, the step-wise approach consisting of four steps in synthesis stage; (1) Problem definition (2) Superstructure generation, (3) Mathematic model and (4) Problem solution.

Superstructure-based process synthesis is an effective way to determine the optimal pathway from a network of alternatives based on an integrated business and engineering framework for synthesis and design of processing networks (Quaglia et al., 2013). An optimal pathway represents the potential integrated process based on defined performance criteria. Process synthesis problem, which involves evaluation of many possible alternative technologies is complex and needs a systematic methodology with support by computer-aided tools for its solution. In this work, the step-wise approach consisting of four steps, as shown in Figure 17 is considered. Steps 1.1 to 1.4 for process synthesis (Stage 1) are detailed below.

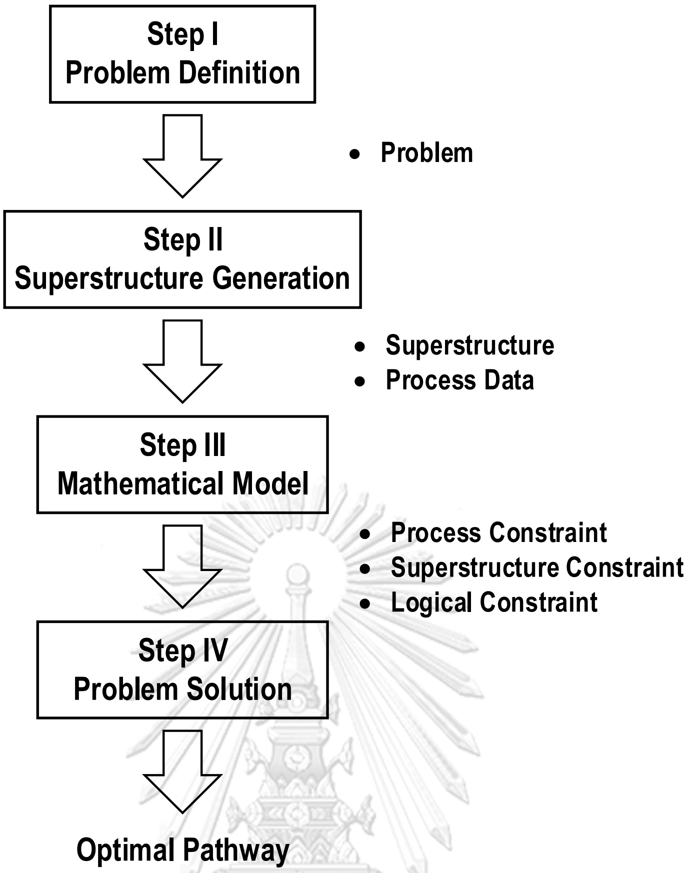


Figure 17 Workflow of superstructure-based process synthesis methodology

3.1.1Step 1.1: Problem definition

First, the synthesis problem is defined. The promising pulp and paper mill to be transformed is selected as a receptor mill. Biorefinery platforms, both biochemical production and black liquor utilization, are considered as the selected receptor mill to share raw materials, by-products, utilities and some facilities. Pulp, that is a product from pulp mill, is exported for paper production and sent to biochemical production as feedstock to produce value-added biochemicals. For black liquor, the conventional process for black liquor treatment is selected as the chemical recovery system. Black liquor utilization technologies are included in the superstructure so that comparisons with the conventional process can be made. The goal is to determine the most promising process pathway for integrated biorefinery in an existing pulp mill with respect to three scenarios that are single product biorefinery in pulp mill (scenario I), biochemical co-production with pulp for paper production (scenario II) and multiple biochemical production (scenario III). The objective function, the performance criteria, process constraints and required data (economic and technical) are defined. Computer aided tools are applied to collect data and solve the synthesis problem. The objective function in this work is to maximize profit, as given by equation (1). The process profit is calculated as the difference of income from product sale and expenditure due to raw material, chemical, utility and capital costs.

3.1.2 Step 1.2: Superstructure generation

A superstructure represents all considered processing routes as possible alternatives in terms of processing steps and intervals (processing technologies that may be used for each processing step), illustrated in Figure 18 (Quaglia et al., 2013). Each processing step consists of associated intervals. The model representing a process interval in the superstructure as shown in Figure 19 consists of operational processing tasks, such as reaction, mixing, separation, or their combination. Interval information on raw materials, main products, side products, reactions, chemical added, utilities and economic data such as product price, raw material cost, chemical cost and capital cost are collected from published articles and scientific reports, available industrial data and databases. Superstructure is generated from processing step and interval information employing, considering integration of biorefinery technologies with the receptor pulping process consisting of pulping process, promising biochemical production and black liquor utilization technologies. Biorefinery technologies are screened in terms of market trends, feasibility and potential developments within the pulp and paper industry. Super-O is an in-house software that is employed to effectively collect a large data for superstructure generation. Detail of Super-O feature are given in Appendix A.

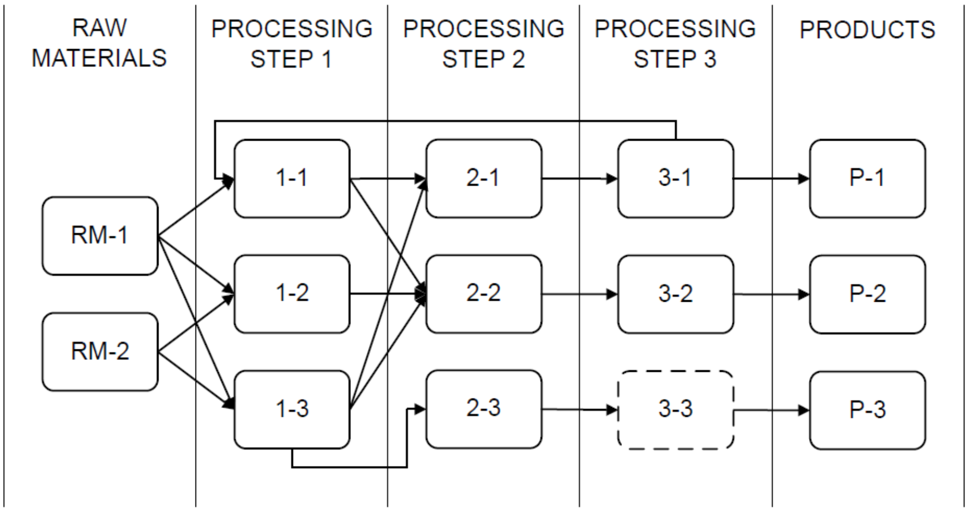


Figure 18 Generic superstructure for a synthesis problem of processing networks illustrating the concepts of processing step (column), processing interval (box), by-pass (box with dotted outline), primary connection (arrow starting from the right hand side of the interval), secondary connection (arrow starting from the top or bottom of the interval) (Bertran et al., 2017)

3.1.3 <u>Step 1.3: Mathematical model</u>

A set of mathematical models is developed and validated to represent the superstructure (see Appendix B). The generic modeling approach that has been proposed in several case studies in process synthesis problems (Zondervan et al., 2011), (Rizwan et al., 2013), (Frauzem et al., 2015) is adopted in this work. Each process interval is represented by the generic mathematical model. The process interval model is defined in terms of component mass balance and energy balance. A series of processing tasks namely mixing of chemical inlet, reaction, waste separation, product separation and used utility are considered for each alternative processing interval. A schematic representation of the generic process interval with representing mass flowrate variables is shown in Figure 19. The mathematical programming problem, process constraints, logical constraints and the variable bounds are formulated as a mixed integer (non)linear programming problem or MI(N)LP model. The consistency of model and data is checked and it is verified that the collected data represents all model parameter values. The superstructure representation also includes a list of decision variables that determine the connections between intervals from one processing step to another. The superstructure generation and data collection is performed through a special software named Super-O, which is an interface for formulating and solving superstructure-based optimization problems (Bertran et al., 2017).

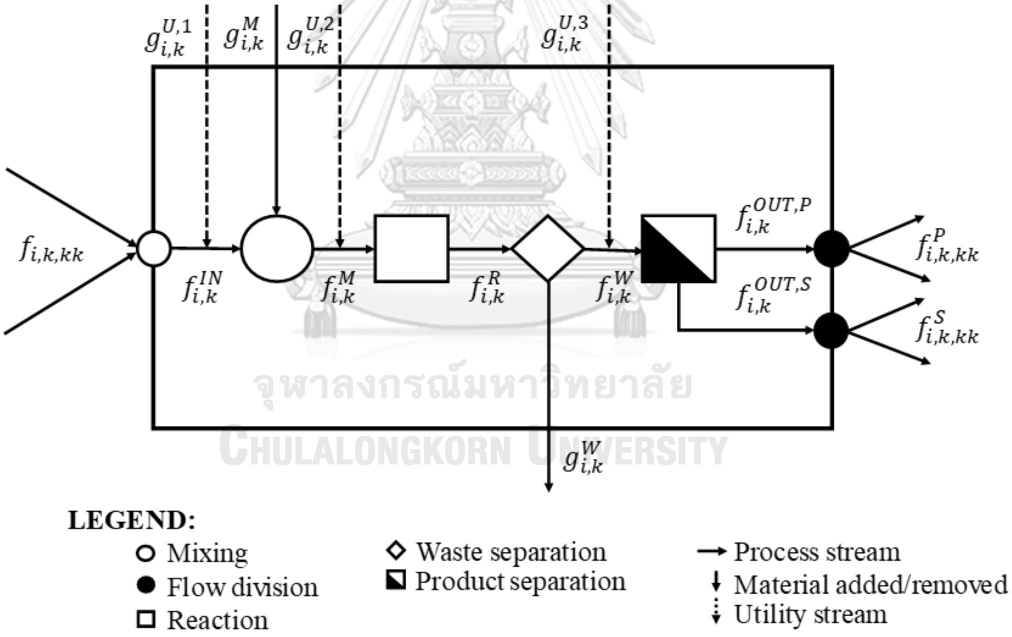


Figure 19 The generic process interval with internal variables

The mathematical model is generated for the constructed superstructure given in general form as

min $\quad Z = f(\bar{x}, \bar{y}, \bar{p})$ (1)

s.t. $$\bar{g}(\bar{x},\bar{y},\bar{p}) \le 0 \quad (2)$$

$$\bar{h}(\bar{x},\bar{y},\bar{p}) = 0 \quad (3)$$

$$\bar{x} \in X^n \quad (4)$$

$$\bar{y} \in \{0,1\}^m \quad (5)$$

$$\bar{p} \in P^l \quad (6)$$

where Z is the objective to be minimized (or maximized), functioned as $f(\bar{x},\bar{y},\bar{p})$, which could be a function of cost, environmental impact, or sustainability index depending on the design purpose. $\bar{g}(\bar{x},\bar{y},\bar{p})$ and $\bar{h}(\bar{x},\bar{y},\bar{p})$ are vectors of inequality and equality constraints respectively. $\bar{x}$ is a vector of continuous processing variables such as flow rates, conditions (temperature, pressure), or equipment sizes lies in a continuous feasible region X^n; $\bar{y}$ is a vector of integer variables representing discreet decisions; and $\bar{p}$ is a vector of processing parameters exists in a parameters region P^l. The regions are defined by the lower and upper bounds of variables and parameters.

The objective function is typically to maximize (or minimize) an economic, environmental, or sustainability aspect which is translated to mathematical model given as

$$Z = C^P + C^{RM} + C^U + \frac{C^{Cap}}{\tau} \quad (7)$$

where C represents cost-impact vectors of products (P), raw materials (RM), utilities (U), and capital investments (Cap) whether they are economic, environmental, sustainability, or mixed impact. These impacts can be either positive or negative depending on the effect of their corresponding production or usage of the materials and energies toward the overall objective.

3.1.4 Step 1.4: Problem solution

The optimization problem with the formulated MILP or MINLP models from step 1.3 are solved with GAMS (IBM Corp, 2009) through Super-O. The developed generic model, namely the user defined objective function, process interval constraints, superstructure flow constraints and logic constraints, and the necessary data are given in an input file. The problem solution is analyzed and recorded for future use.

In general, the problem formulated with lower degree of uncertainty can be solved directly with the mentioned solvers. However, due to time and computational constraints, solution strategy is needed for the problem with higher degree of uncertainty. A bi-level decomposition algorithm (Nishi et al., 2011) has been adopted for speeding up the solution step. The algorithm decomposes the optimization problem into two layers, the upper layer is a relaxed version of the original problem and is solved for a lower bound; the upper layer is a problem with some fixed decision variables from the lower layer; both layers are solved iteratively while cuts are affixed, until the termination criteria is met. The algorithm procedure is illustrated in Figure 20.

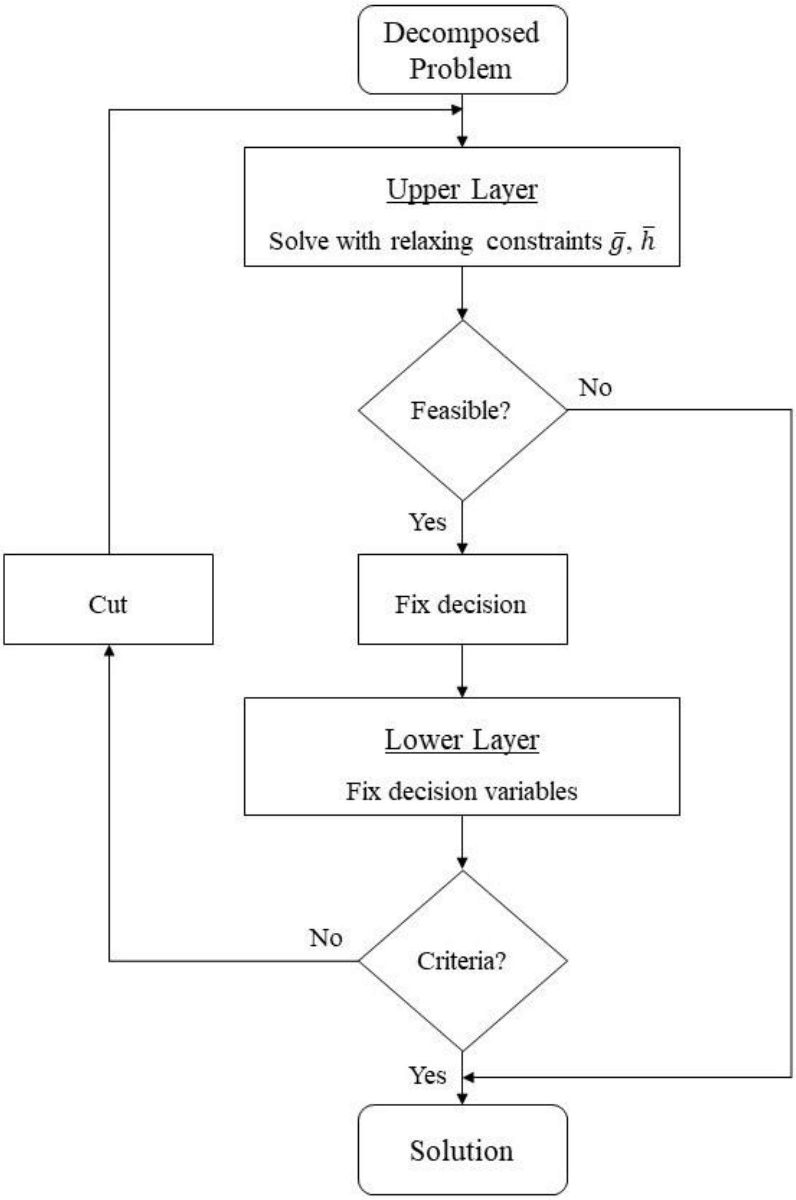


Figure 20 Bi-level decomposition algorithm

The outputs from the solver are the optimal values of the objective function and all design and process variables. The solution, containing the optimum processing route and the raw materials and products sections, is carried to Stage II (Design) for further analysis; on the contrary, it can be solitary used if no extra detail is required.

3.2 Stage II: Design

Objective of stage II: Process design and setting target for improvement

Method: Process simulation and evaluation

Outputs: Rigorous flow sheet of base case

Information of sustainability assessment in term of economic, environmental and/or social impact.

Improvement gaps and targets

Supporting software: Aspen Plus (Process simulator), LCsoft (Life cycle assessment (LCA) analyzer) (Kalakul et al., 2014), ECON (Economic database) (Saengwirun, 2011), and Sustain Pro (Sustainability analyzer) (Carvalho et al., 2013)

Concept: The promising networks of optimal pathways from synthesis results (stage I) are opted as base cases to be further designed and evaluated in this stage. The process models are complex to accurately describe the process configuration and performance. Detailed flowsheet is constructed by base case simulation to obtain more rigorous process information such as mass and energy balances, equipment sizing, operating conditions. The detailed information of process performance leads to defining bottlenecks of the base case though evaluation in terms of economic, energy consumption, environmental impacts. Therefore, targets for improvement can be specified to debottlenecks or minimize the process hot-spots. This design stage is proceeded by three steps; (1) Base case design, (2) Process simulation, (3) Process evaluation, and (4) Improvement targeting.

3.2.1 Step 2.1: Base case design

One or more promising processes from synthesis stage are established as base case. The basic configuration of base case is designed and adopted technologies are specified. Then, processing criteria and conditions such as feed information, required chemical, reaction kinetics, operating temperature and pressure, separation technique and other equipment parameters are obtained from literature, plant data, simulation reports and design calculation.

3.2.2 Step 2.2: Process simulation

Following the basic design of base case configuration, process simulation is supported by design software, which is Aspen Plus® simulator for this study. The detailed flowsheet is simulated with processing information on the streams and equipment. The process simulations are typically performed by definition of all associated components, appropriate thermodynamic models which can represent the behaviors of presented species and their interaction, equipment models and required processing parameter, for example, feeds and products information, process topology, operating conditions, reaction conversions and yield or defined kinetic models with related parameters, separation efficiency, equipment sizes. These necessary parameters are obtained from literatures. Detailed information on the streams and equipment is calculated by employed simulator and then forwarded to the next step for analysis.

3.2.3 Step 2.3: Process evaluation

The base case is evaluated by the detailed stream and equipment information from step 2.2 in terms of economic aspect, energy consumption and environmental impact that is generally gauged by LCA factors so that process deficiencies can be found out. The economic efficiency is simply indicated by total profit and/or a cost of operation per unit of product, while a common life-cycle assessment is net carbon dioxide emission. To reveal the potential for improvement, process analysis is supported by commercial software, however, in-house computer-aided tools are developed and employed by many studies (Babi et al., 2015; Kongpanna et al., 2016; Bertran et al., 2017). For example, emission of greenhouse gases can be imposed by LCsoft, economic information is acquired from ECON and/or SustainPro can analyze process sustainability providing the insight on the improvement feasibilities.

3.2.4 Step 2.4: Improvement targeting

These hotspots are located by the highly potential for improvement area. The base case design with the improvement feasibilities can be forwarded to stage III for innovation developments. Alternatively, the result can be solely used if process improvement is found not necessary or the targets for improvement are subjected for the developments in the future.

3.3 Stage III: Innovation

Objective of stage III	Innovation for process improvement
Method	Process contribution and/or process intensification
Outputs	Innovative alternatives Improvement channels Sustainable process
Supporting software	ProCAFD for Process intensification (Tula et al.,2017)
Concept	The innovation stage involves two main tasks; alternative generation and evaluation. In this final stage, sustainable developments are expected to receive the better process than

base case. Depending on process analysis along with improvement targets, the innovative processes can be generated as alternatives by enhancing strategies that typically are process contribution and/or process intensification. Alternatives for more sustainability rely on available technologies and development purposes. After all, created alternatives are evaluate in term of assessments which relate to improvement concerns. Then, results of their performances are compared with the base case to opt for effective alternatives and obtain the best sustainable pathway achieving the improvement targets. Although innovation stage can be omitted, it is a key stage for enhancing sustainability of the existing base case to get a better process.

3.3.1 Step 3.1: Alternative generation

The innovation stage begins with alternative generation for base case development that achieve the improvement targets. The innovative alternatives can be created by one or more techniques so that process performances meet the improvement targets.

Process intensification is an approach to design the possible innovation such as new hybrid equipment. The phenomena-based process intensification method proposed by Lutze et al. (2013) and extended by Babi et al (2015) is a step-wise process intensification that can design innovative equipment with traditional operating tasks. With expectation of reducing unit size, energy consumption, emission and/or waste, the innovative unit can be intensified by re-combining tasks of traditional unit operation into new feature of unit operation. However, the operating performance, limitation and all constraints are kept constant except the set targets. If intensified alternatives are more than one, they are considered only alternatives which are related to the specified targets. The intensified operations achieving the improvement targets provides more sustainable process than the base cases. Process intensification approach has been employed in several applications (Lutze et al., 2013; Babi et al., 2015; Babi et al., 2016; Kongpanna et al., 2016) In addition, a computer aided tool for automatic process intensification has been developed by Tula et al. (2017) as an extension of ProCAFD software.

Process integration is the way to improve the existing process by addition of external process and engaging multiple operation together, or energy and material integration between operating unit. Heat exchanger system should be initially considered as well as the integrated supply chain (Chen et al., 2009). Moreover, the special technology also can be retrofitted into the existing process or replace the traditional process to receive the opportunities for better process based on the targets.

3.3.2 Step 3.2 Alternative evaluation

The innovative alternatives that are generated and screened in step 3.1 are further evaluated in the concerned aspects normally in terms of energy consumption and environmental impact. Base case design is also imported in this step to compare with the considered alternatives. By this way, it can define the best alternative based on the targets which have been established as improvement goal. A sustainable process is finally specified to be development manner overcoming drawbacks of the traditional process.

CHAPTER 4

INTEGRATION OF THE BIOREFINERY CONCEPT FOR THE DEVELOPMENT OF SUSTAINABLE PROCESSES FOR PULP AND PAPER INDUSTRY

This chapter aims at identifying a promising process pathway for a biorefinery integrated with an existing pulp mill considering different operational objectives (scenarios). The developed superstructure consists of three main sections, which are pulping section as the receptor, the biochemical production section and the black liquor utilization section. The three scenarios considered, include pulp for paper production and biochemical production as alternatives (scenario I), biochemical co-production with pulp for paper production (scenario II) and multiple biochemical production (scenario III). The appropriate integrated network for each scenario is determined.

First, the collected processing information is given. Then the generated superstructure of the biorefinery integrated with a pulping process involving three main sections (pulping process, biochemical production and black liquor utilization) is introduced. With Super-O in-house software, superstructure with technical and economic process information is collected and formulated as input file in form of Excel file. For optimization solution, Super-O interface with GAMS solve define the optimal processing pathway and generate the results as output file in form of Excel file. Input file of superstructure in this case is partially provided in Appendix C. The results from the superstructure optimization are given and analyzed for the three scenarios to determine optimal networks. Optimal networks for each scenario are compared with stand-alone pulping process and other pathways.

4.1 Collected processing information

Processing information was collected to generate the superstructure of integrated biorefinery in pulping process. The information includes pulping process with different raw materials, biochemical process and black liquor utilization process.

4.1.1 Pulping process

Kraft process is the dominant chemical pulping technology in today's pulp and paper industry due to several advantages over other pulping processes, namely, good strength properties of pulp, ability of the process to handle a wide range of raw materials (mostly softwood and hardwood) and high efficiency of chemical recovery (about 97%) leading to economic benefits (Tran and Vakkilainnen, 2015). The Kraft process with a cooking chemical recovery system is employed as a receptor pulp mill for the integrated biorefinery network. Hardwood from Eucalyptus tree is used as raw material. First, they are fed to the feedstock pretreatment section consisting of debarking and chipping operations. Debarked wood chips are digested with a solution of cooking chemicals composed of sodium hydroxide ($NaOH$) and sodium sulphide (Na_2S) at 150-170°C and 110-150 psi. The feedstock is allowed to stay one to three hours to complete the cooking reaction that breaks the bonds linking lignin, hemicellulose, and cellulose. Lignin is dissolved from crystallized cellulose fibers by this process. The product from the digester is sent to pulp washer where the spent cooking liquor called black liquor (the spent cooking chemical with mainly lignin, hemicelluloses and degradation products from carbohydrates) is separated from unbleached pulp fiber (mainly cellulose). Black liquor (the used cooking chemical) is regenerated to cooking chemicals ($NaOH$ and Na_2S) called “white liquor” via a chemical recovery system for reuse at digestor. For printing paper production, removal of more lignin as well as destroying the coloured groups in lignin and removal of impurities, such as resin by O_2 delignification, from the pulp are carried out before pressing and drying into the finished product.

Due to economic viability on a small scale, Soda process is the preferred method of chemical pulping process that employs only NaOH as the cooking chemical without Na_2S to utilize non-wood biomass for pulp production. Agricultural residues such as sugarcane bagasse and wheat straw are important raw materials for non-wood pulping processes in agricultural countries or counties with a shortage of wood such as India and China. Nowadays, non-wood pulp utilized is around 10% of the total chemical pulp produced in the world (Doherty and Rainey, 2006). Chemical bagasse pulp can be mixed with wood pulp to produce newsprint, toilet paper, serviettes, cardboard for food container or packaging.

4.1.2 Biochemical process

Biochemical processes have potential to be integrated with pulping process because pulping feedstock can also produce the wide range of biochemicals that are considered as sustainable chemicals replacing petrochemical. The promising biochemicals reported by DOE's report as well as developed in commercial scale were considered for integration with pulping process.

- *Ethanol*

Ethanol is reported as a revisited platform biochemical in 2010 although it was omitted by DOE's report in 2004 because of limited application as fuel (Bozell and Petersen, 2010). From the market size of 86 million tons of ethanol per year, most of ethanol application has been as a fuel additive while only 18% is employed for non-fuel applications (Harmsen et al., 2014). Due to recent technology developments and strategic commercial partnerships, bioethanol also has been considered as a building block biochemical for various derivatives and not just employed as a fuel. By vapor phase dehydration of ethanol with extremely high conversion (99.5%) and selectivity (99.9%) in fluidized bed reactors over activated alumina, bioethanol can be a precursor for ethylene production (Morschbacker, 2009). Several companies such as Braskem, Dow Chemical–Mitsui Chemicals, and Solvay have commercialized bio-based ethylene production (Choi et al., 2015). Ethylene has the largest market size among petrochemicals, with over 150 million tons in 2016 (Research and Markets, 2016). It is a primary petrochemical that can be converted to a diverse range of polymers such as polyethylene (PE), polyethylene terephthalate (PET), polyvinylacetate (PVA), polyvinylchloride (PVC), and many others.

Initially, bioethanol has been produced by fermentation of sugarcane, sugar beet and starch crops that are defined as raw materials in competition with food and feed industries. Then, bioethanol production from non-food biomass is expected to overcome the limitations on feedstock competition. Bioethanol production from lignocellulosic feedstock has been reported by the National Renewable Energy Laboratory (NREL) where lignocellulose biomass is pretreated with dilute acid followed by hydrolysis with Cellulase as the enzyme (Wooley et al., 1999).

- *Lactic acid*

Lactic acid is one of the promising biochemicals mentioned in report 2010 due to its wide range of application (Bozell and Petersen, 2010). The market size of the lactic acid is about 400,000 t per year (Choi et al., 2015). Most of produced lactic acid has been used for polylactic acid (PLA) production. The demand of PLA has driven the market growth of lactic acid. Bio-based lactic acid and polylactic acid has been manufactured in commercial scale by many companies. PLA has potential to be alternative biopolymer for polyethylene terephthalate (PET) from petrochemical. Thus, it can be considered a platform chemical for future plastic production, for example, plastic bottles (Janssen, 2013). Moreover, lactic acid can be a precursor for the production of a wide range of chemicals such as acrylic acid, 1,2-propanediol, acetaldehyde and 2,3-pentanedione (Fan et al., 2009).

Bio-based lactic acid is produced by the fermentation of sugars. Lactic acid bacteria, such as *Lactobacillus*, *Lactococcus*, and *E.coli* strains can offer high lactic acid yield at pH condition of 5~7 and temperature of 35~45°C. An engineered bacterium, *Lactobacillus,* is mostly used in the commercial production of lactic acid due to its tolerance in acidic condition and good selectivity (Lee, 2015).

- *Succinic acid*

Succinic acid is as one of the top 10 bio-based chemicals in The U.S. *Department of Energy's* report since 2004 along with 2010 when the report was revised (Bozell and Petersen, 2010). Succinic acid is an important platform chemical which has been used in various applications such as food, pharmaceutical, cosmetic and polymer. It is being produced from petroleum-based chemical, maleic anhydride. However, bio-based succinic acid is considered as potentially competitive with the petroleum-based. In 2014, the market size of succinic acid was rather small, at about 30,000-50,000 MT per year because many valuable derivatives of succinic acid could be directly produced via the petrochemical pathway without the succinic acid route (Choi et al., 2015). With the production technology of biomass-derived succinic acid being developed to overcome its conventional production, bio-succinic acid is now considered as a key building block chemical instead of the petrochemical derived one, causing growth of the market to a size of about 180,000 MT per year (Pinazo et al., 2015). It has been expected for the market size to grow to about 699,449 MT in 2020 (Weastra, 2016). Main producer companies for the bio-based succinic acid are: Reverdia (joint venture of DSM and Roquette), Succinity (joint venture of BASF and Corbion Purac), Bioamber (joint venture of DNP Green Technology and ARD) and Myriant who already have commercialized the process (Choi, 2015). Succinic acid can be used as a precursor to produce a range of valuable products e.g. 1,4-butanediol (BDO), tetrahydrofuran (THF) and γ-butyrolactone (GBL) by direct hydrogenation (Cukalovic and Stevens, 2008). BDO is an important chemical for polymer production, polyesters, polyethers and polyurethanes. BDO has potential to be the biggest market for succinic acid as well as Polybutylene succinate (PBS) synthesized by direct esterification of succinic acid with 1,4-butanediol (Weastra, 2016). PBS can potentially be an alternative biodegradable plastic that has similar physical properties as polyethylene terephthalate (PET). Several companies have established the commercialization of the bio-based PBS production (Choi et al., 2015).

Production of succinic acid has been demonstrated using several microorganisms such as *Actinobacillus succinogenes* (Guettler et al., 1999), *Mannheimia succiniciproducens* (Lee et al., 2002), *Corynebacterium glutamicum* (Okino et al., 2005), *Anaerobiospirillum succiniciproducens* (Lee et al, 2003) and *Escherichia coli* (Donnelly et al., 1999). At 37~39 °C, pH 6~7.5, in presence of CO_2, *Anaerobiospirillum succiniciproducens* can produce succinic acid with high yield from renewable sources like wood hydrolysate which is the mixture of C5 and C6 sugars (Lee et al., 2003). Several methods of biosuccinic acid purification have been reported including precipitation (Guettler et al., 1998), reactive extraction (Glassner et al., 1995), direct vacuum distillation with crystallization (Luque et al., 2009), and electrodialysis

(Kurzrock and Weuster-Botz, 2010). Recently, one-step succinic acid recovery method by direct crystallization was proposed by Li et al. (Li et al., 2010).

4.1.3 Black liquor utilization

Black liquor is spent cooking liquor separated from pulping line to send to a chemical recovery system. The chemical recovery cycle is desired to recover and reuse cooking chemicals that make the pulping process economically feasible and environmental friendly. Black liquor consists of inorganic spent cooking chemicals and organic compositions that are separated from pulping raw material. The black liquor solids contain more than a half of organics in biomass fed into the digester. Therefore, the chemical recovery system is not only used for cooking chemical recycle, but also performs biomass combustion of organics as an energy supply system for pulping process.

- *Tomlinson boiler (Conventional process)*

Tomlinson boiler is a traditional recovery boiler in pulping process invented by G.H. Tomlinson in the early 1930s. The invention was a milestone in the advancement of the Kraft process. The recovery boilers can perform dual functions; i.e. energy generation from combustion of organic compounds and pulping inorganic chemicals recovery. Although the traditional recovery process with Tomlinson recovery boiler has proven to work well, there are several major disadvantages; e.g. low electricity generation efficiency and smelt-water explosions (Naqvi et al., 2010). New technologies including black liquor gasification that offer more efficiency and economic benefits has been developed to overcome and replace the conventional recovery boilers more to offer in terms of efficiency and economic benefits (Larson et al., 2006a).

- *Black liquor gasification combined cycle*

A black liquor gasification combined cycle (BLGCC) integrated with the pulp mill has shown a potential to achieve higher energy efficiency than the conventional recovery system (Larson et al., 2003), (Eriksson and Harvey, 2004). Syngas is produced from black liquor gasification and utilized for energy generation. Energy assessment and economic information of BLGCC technology was reported by Larson et al. (2003). The commercial viability of BLGCC integrated with the pulp and paper industry in the long term was assessed along with the comparison of conventional Tomlinson boiler.

- *Black liquor gasification with DME production (BLG/DME)*

Not only BLG can offer more efficient power supply, but it can be integrated with biofuel production that has potential for the replacement of fossil fuels. Biofuel can also be a high value co-product with pulp to improve profit as well as environmental improvement. Biofuel production routes require very clean synthesis gas because impurities like H_2S, CO_2 can offer catalyst poisoning. The total energy deficit of the pulp mill with biofuel production can be fulfilled by hog fuel, both purchased wood and existing bark, or other resources. BLG with biofuel production is similar to BLGCC but with certain synthesis gas conditioning. The synthesis gas reforming, shifting and CO_2 separation is required before biofuel conversion (Naqvi et al., 2010).

DME is potentially a substitute for liquefied petroleum gas (LPG, a mixture of propane and butane) used as fuel in household and industry. Due to its high cetane number of 55, it is also an excellent fuel in diesel engines, petrol engines (30% DME/70% LPG), and gas turbines. The simplicity of its short carbon chain leads very low emissions of NOx, and CO during combustion. DME as vehicles fuel has been paid attention from worldwide (New York and Geneva, 2008) Although a complete replacement for LPG needs to change the burners due to the difference in calorific values between LPG and DME, mixtures of DME and LPG limited to 15-25% by volume of DME can be applied the LPG combustion equipment without changes (Anggarani, 2014).

- *Lignin extraction*

Most lignin in pulping feedstock is removed as black liquor, together with spent cooking chemicals. It is burnt in a recovery boiler to provide energy for the pulp mill. Lignin has been proposed as a versatile platform for production of biofuel, biomaterial and even biochemical building blocks (Bozell et al., 2007). Lignin extraction from black liquor can drive fossil-free pulp mill. It can be used as solid fuel in lime kiln process replacing fossil fuel oil (Tomani et al., 2011). Considering a long-term development, there is a great potential that lignin will become a valuable building block for integrated biorefinery platforms in future. Even though steam production in the recovery boiler is decreased when lignin in black liquor is extracted due to the reduction of the energy resource, the pulp production capacity is increased because of off-loading the recovery boiler that is a debottlenecking method. When pulp mills need to increase the production capacity, the recovery boiler is the bottleneck for the pulping process.

Several methods for lignin extraction have been reported; extraction with organic solvent (Li and McDonald, 2014), ultrafiltration by membrane technology (Wallberg et al., 2003), (Toledano et al., 2010) and fractionation by acid precipitation (Garcia et al., 2009), (Wang & Chen, 2013), (Santos et al., 2014), (Lourencon et al., 2015). Acid precipitation technology using CO_2 as a precipitating agent (Zhu, 2015) has been the most promising approach for lignin extraction in terms of yield and cost (Benali et al., 2014), (Sharma et al., 2015). Lignin precipitation has been commercially available by

Chalmers University of Technology and Innventia AB and today owned by Metso. The process is called LignoBoost. The black liquor is separated as a side stream from the black liquor evaporation plant. The technology is based on lignin precipitation by acidification, preferably with CO_2, and filtration (Tomani et al., 2012). The filtrate after lignin extraction is recycled to the black liquor evaporation plant. The LignoBoost process is claimed that it provides the fast production of high-quality lignin at a low cost (Sherma et al., 2015).

4.2 Superstructure Generation

The Kraft process and the Soda process are selected as receptor pulping processes. Biorefinery technologies that have potential to be integrated with pulping processes are selected including biochemical platform for biochemical production and thermochemical platform for black liquor utilization. Top value-added biochemicals considered in this study are succinic acid, lactic acid and ethanol. For the thermochemical platform, black liquor gasification is included in the generated superstructure. The superstructure consists of 71 processing intervals, divided into 16 steps of operations. The information related to the superstructure optimization problem is given in Table 4. Two types of raw materials, eucalyptus wood and sugarcane bagasse, are converted to nine types of final products: Kraft unbleached pulp, Soda unbleached pulp, ethanol, lactic acid, succinic acid, process steam from hog fuel combustion, electricity, dimethyl ether and lignin fuel. Overview of the superstructure of alternative networks for scenario-based optimization is illustrated in Figure 21, along with intervals for the biochemical production in Figure 22.

Table 4 Statistics of the superstructure optimization problem (Abbreviations as follows: NI is the number of processing intervals; NF is the number of feedstocks; NP is the number of products; NC is the number of components; NR is the number of reactions; NEQ is the number of equations; NV is the number of variables)

Problem	NI	71
	NF	2
	NP	15
	NC	51
	NR	55
Model and Solver	NEQ	825,633
	NV	812,856
	Problem type	MIP
	Solver	CPLEX

4.2.1 Overview of Superstructure

The Kraft process, where eucalyptus is a raw material, and the Soda process with bagasse as a raw material are selected as receptor pulp mill configurations. Biochemical processes employing pulp and bark (a by-product from the eucalyptus process) and pith from sugarcane bagasse, produces potential products for the biochemical market consisting of ethanol, lactic acid and succinic acid. Alternatives to the pulp pathway are to market pulp for paper production and as feedstock for biochemical production. Simultaneously, bark and pith, pulping by-products, can be fed to biochemical processes with a pretreatment step or employed for process steam production. Black liquor from the pulping process is utilized for energy and biofuel production that are supplied to the pulping process and for sale. Three technologies including black liquor gasification combined cycle (BLGCC), black liquor gasification for dimethyl ether production; (BLG/DME) and lignin extraction (LE) are considered as efficient processes to replace the conventional process, Tomlinson boiler. For all black liquor utilization technologies, the generated steam and electricity is supplied to meet the pulping process demand. The excess electricity is sold to grid while any deficit electricity is purchased. Regarding DME production, the process can supply energy for the pulping section with DME production for sale. Lignin extraction is designed to supply extracted lignin as biofuel to substitute fuel oil from petroleum in the lime kiln operation. Incomes from extra pulp productivity due to lignin extraction are also considered.

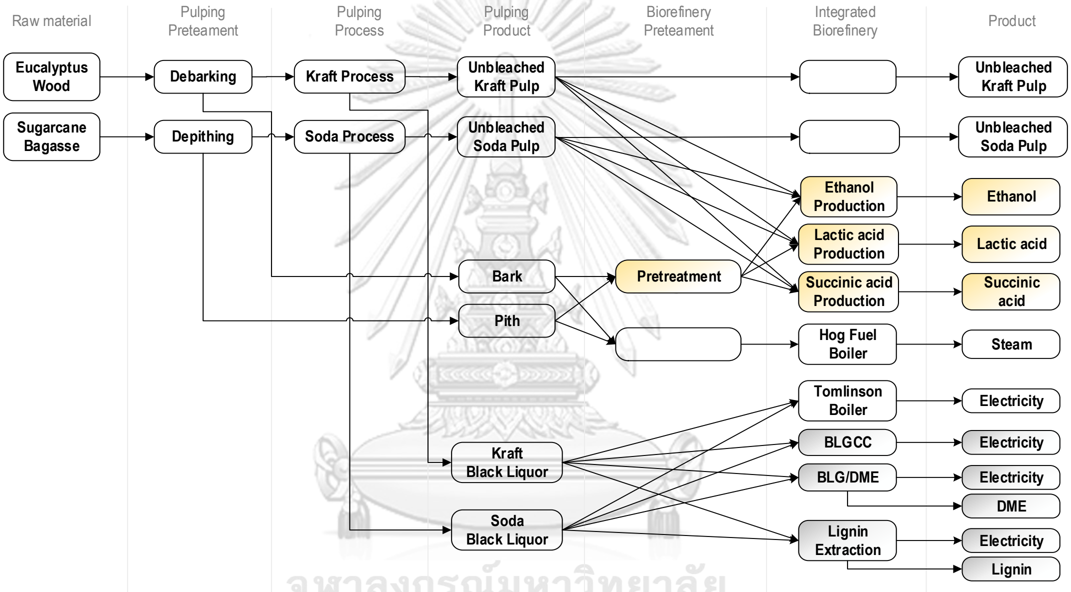


Figure 21 Overview of superstructure for integrated biorefinery network

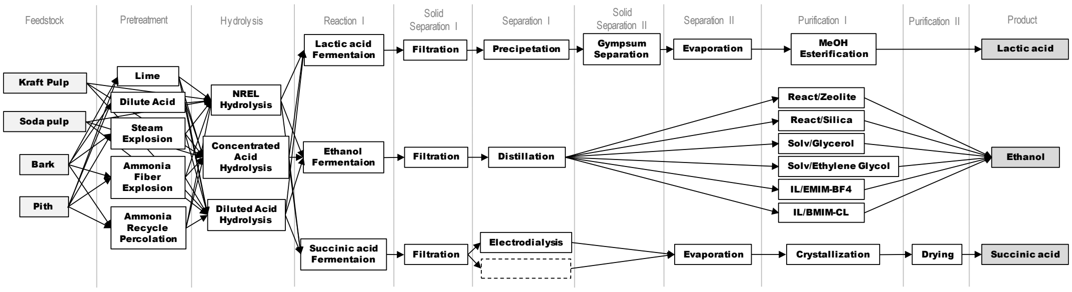


Figure 22 Superstructure of biochemical production

4.2.2 Pulping process

- *Kraft process*

In the superstructure, unbleached pulp is considered as product export for paper production and feedstock for integrated biochemical production. Barks, by-products from wood pretreatment, are fed for biochemical production with pretreatment step. The yield for unbleached pulp production with Kraft cooking process is 45% based on debarked eucalyptus wood chip. The flow-diagram of the Kraft process is displayed in Figure 23.

- *Soda process*

In the superstructure, sugarcane bagasse is selected as a feedstock for the Soda pulping process as it is widely used commercially. Bagasse is pretreated to remove pith in depithing step before digestion with sodium hydroxide as a cooking chemical. Pith is exported to the biochemical production section as feedstock. Depithed bagasse is transferred to the digesting process for delignification. The yield for unbleached pulp production with the Soda cooking process is 50% for depithed bagasse. Black liquor containing the spent cooking chemical and extracted organics from pulp fiber is removed from pulp at the washer and then sent to a chemical recovery system. Pulp fiber is sent to a screener and then to a thickener before becoming unbleached Soda pulp that is sold to paper production and alternatively used as a feedstock for biochemical production. The configuration of the Soda cooking process is illustrated in Figure 24.

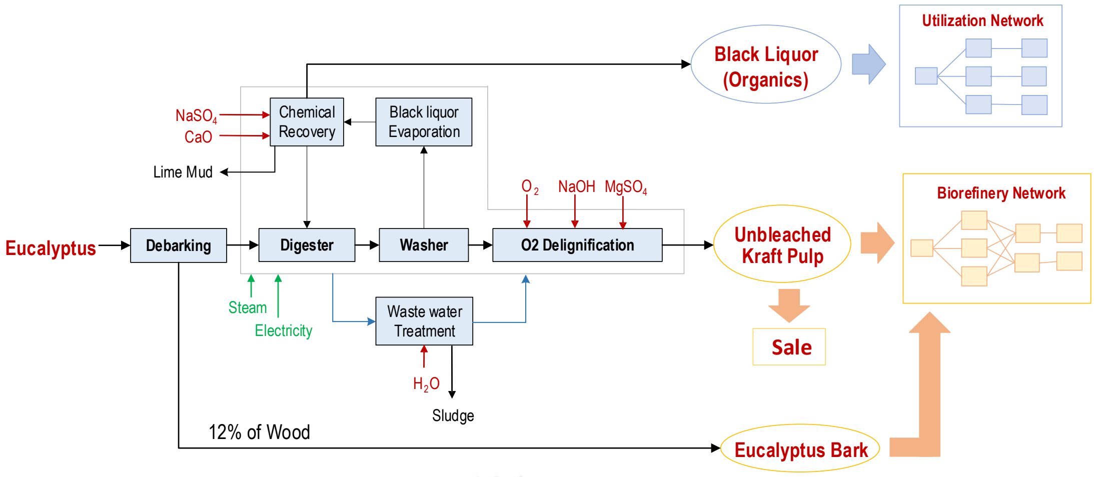


Figure 23 Kraft process configuration with biorefinery-integrated pathway

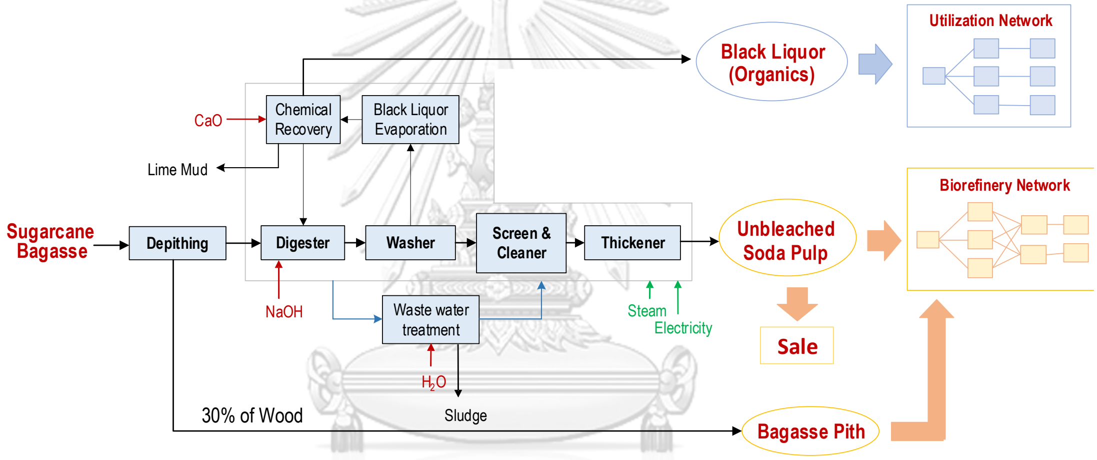


Figure 24 Soda process configuration with biorefinery-integrated pathway

4.2.3 Biochemical process

After pulping process, pulping products are sent to the implemented biochemical production section. Unbleached pulps and lignocellulosic by-products namely bark, and pith are firstly sent to pretreatment and hydrolysis steps for fermentable sugars. Pulps mainly consisting of cellulose are directly fed to the hydrolysis step, whereas, bark and pith that is lignocellulose need pretreatment step before hydrolysis. Pretreatment technologies include pretreatments with lime, dilute acid, steam explosion, ammonia fiber explosion and ammonia recycle percolation.

Hydrolysis step could be alternatively enzymatic hydrolysis with NREL enzyme, concentrated acid hydrolysis and dilute acid hydrolysis. The choices of pretreatment and hydrolysis technologies directly affect conversion, selectivity, capital cost and operating cost.

- *Ethanol*

Ethanol production in the superstructure includes fermentation, separation and purification steps. After the feedstock from pulping process is preteated and hydrolysed into sugars, they are converted to ethanol by yeast, Zymomonas mobilis in fermentation step. For the separation step, filtration is used to remove solid waste, after that, beer distillation takes place to get 95% ethanol with water. Purification steps are required to get high purity of ethanol (99% in weight). Several purification methods were included as alternative pathways for bioethanol production (Alvarado-Morales et al., 2009), (Zondervan et al., 2011). Different solvent-based extraction alternatives are considered: with ethylene glycol and glycerol; liquid-liquid extraction with ionic liquids EMIMBF4 (1-Ethyl-3-methylimidazolium tetrafluoroborate) and BMIMCl (1-Butyl-3-methylimidazolium chloride); rectification column followed by silica membrane, and rectification column followed by zeolite membrane, as shown in Figure 22.

- *Lactic acid*

Bio-based lactic acid is produced by the fermentation with *Lactobacillus.* After fermentation, the conventional method of lactic acid recovery is employed for lactic acid production in the superstructure. Precipitation is a conventional separation method widely used for lactic acid separation (Lee, 2015). Normally, a neutralizing agent such as calcium carbonate ($CaCO_3$) is added in the fermenter to control pH at 5~7 causing the formation of a lactate salt, so lactic acid is more likely to be a form of lactate salt, e.g. calcium lactate, than free lactic acid. After fermentation, solid waste and cells are removed through a filter. Calcium lactate is converted to lactic acid by adding sulfuric acid in the precipitation step where gypsum is created as a by-product. Afterward, the insoluble gypsum is filtered before evaporation step. Esterification, distillation and hydrolysis are finally performed to achieve high purity of lactic acid as the purification step. Methanol is used as a purifying agent added in this step. Purity of lactic acid can reach 99 wt.% after purification by methanol.

- *Succinic acid*

For succinic acid production in the generated superstructure (see Figure 22), direct crystallization with electrodialysis and without electrodialysis are employed as intervals for the purification step after fermentation by *A. succiniciproducens* strain (Lee, 2015). Sodium hydroxide is added in the fermentation step as a neutralizing agent. Cells and solid wastes in the fermentation broth are removed at a filter. Then the liquor is sent to an evaporator where most of the water and lower boiling point by-products which have lower boiling point than succinate like sugars, acetate and formate are vaporized. Afterward, the bottom stream containing a concentrated succinate is fed to a crystallizer where pH is controlled at 2.0 by adding HCl and cooled down to 4°C, the solubility of succinic acid drops to only 3% whereas the solubility of by-products; formic, lactic and acetic acid is still larger. Only succinic acid is crystallized to separate from the rest of impurities e.g. acetic acid and formic acid that can be soluble in water at this condition. Finally, the crystallized succinic acid is further dried to get high purity of succinic acid (up to 99% in weight). In case of the crystallization with electrodialysis, the electrodialysis step takes place before evaporation and crystallization. An electrodialysis separator is applied for base (NaOH) recycle and simultaneously converting succinate to succinic acid.

4.2.4 Black liquor utilization

In the superstructure, black liquor from pulping process is sent to black liquor utilization section involving the promising black liquor utilization technologies that are considered to compare with conventional process.

- *Tomlinson boiler (Conventional process)*

For the effective combustion, black liquor needs to be concentrated from a dilute solution (15-20% solids fraction) to one with a solid content of nearly 80% using multiple-effect evaporators. The concentrated black liquor is then burned in a Tomlinson recovery boiler. Due to extremely high alkali content of black liquor and very conservatively selected steam parameters, the advanced recovery boilers operating at steam temperature close to 500°C is well below than other advanced boilers (Naqvi et al., 2010). The organics in black liquor are completely oxidized to provide heat for high-pressure (HP) steam generation. The HP steam is expanded in a back-pressure steam turbine to generate electricity. The lower-pressure steam is demanded in two levels i.e. medium pressure (MP) at 10–12 bar and low pressure (LP) at 4–5 bars. Steam from the Tomlinson boiler, together with steam from the hog fuel boilers provides for the pulp mill's operation. The generated electricity is supplied a fraction of the pulp mill's electricity demand. The missing electricity, because the amount generated from black liquor and hog fuel is not sufficient, must be also purchased from external utility. For chemical recovery, sodium and sulfur are recovered as molten smelt, mainly composing of sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3), at the bottom of the recovery boiler. The smelt is then dissolved in water to become green liquor which is later regenerated to white liquor with calcium oxide (lime) in a causticizing plant. Calcium carbonate ($CaCO_3$) produced from causticizing process is calcined to regenerate to calcium oxide in the lime kiln using external fuel, e.g. fuel oil or natural gas.

- *Black liquor gasification combined cycle*

In this system, high-temperature BLGCC, designed around a technology being developed by Chemrec Company (Sweden) (Nilsson, 2009) was employed as one of alternative technologies for black liquor utilization in the superstructure.

Black liquor is fed to a gasifier with 95% of oxygen for synthesis gas production (the main components of which are CO, H_2, CO_2, and also some H_2S), together with a molten inorganic stream (smelt, containing primarily sodium and sulfur compounds). At lower section, the smelt is cooled and dissolved to form green liquor, which is sent to causticizing plant for chemical recovery. The hot raw gas is also cooled at a syngas cooler. The synthesis gas obtained after BLG has similar composition to the one obtained from coal or oil gasification (Naqvi et al., 2010). Because the sulfur needs to be recovered to the pulping process, H_2S in syngas must be removed by available commercial process that absorbs the acid gases into solvents via chemical or physical processes. The sulfur-free syngas is fired in gas turbine to generate electricity. Then, the flue gas from the gas turbine passes to a heat recovery steam generator (HRSG) producing high, medium and low-pressure steam. Steam supplement from the hog fuel boiler (fired with existing bark and additional biomass) is need since high-pressure (HP) steam generated from HRSG is not sufficient. Total HP-steam is used in a back-pressure steam turbine to produce more electricity and process steam at lower pressure.

- *Black liquor gasification with DME production (BLG/DME)*

For DME production with black liquor, single-step DME synthesis reactors typically utilize a mix of two catalysts for synthesis of methanol from syngas and dehydration of the methanol to DME. Both liquid phase and fixed bed reactors are employed commercially. Regarding the product separation area, a series of flash tanks separates most of the unconverted synthesis gas from DME, methanol and water. Further separation of the liquid products is achieved by cryogenic distillation. The final DME product has a purity of 99.8%.

In the superstructure, BLG with DME production involves three alternative routes; DMEa, DMEb and DMEc, for optimization. Process information is collected following Larson et al. (2006a). In the DME process design, a liquid-phase DME reactor is performed to convert the synthesis gas from the black liquor gasifier. In case of DMEa and DMEb but not DMEc, 97% of unconverted synthesis gas, separated from product DME, is recycled to the DME synthesis reactor for enhancing DME production. The 3% purge gas from recycle stream is fed to burn with wood residues in the hog fuel boiler for pulp mill's process steam generation. The steam is expanded through a back-pressure turbine to generate some electricity. The deficit of electricity needs to be imported from the grid that is larger than with the conventional Tomlinson boiler process because most of energy is in liquid fuel. For DMEb and DMEc, woody biomass gasification and a gas turbine – steam turbine combined cycle (GTCC) replace the hog boiler and the steam turbine in DMEa. The GTCC is characterized by a higher electricity to steam production ratio than the boiler/steam turbine system in DMEa, more biomass must be used in the DMEb design than in the DMEa design to deliver the same amount of process steam, but electricity production with DMEb is considerably greater than with DMEa. Net electricity production increases since the consumption of wood residues and the efficiency are increased. To enhance electricity generation, more unconverted gas is available for power generation by eliminating the syngas recycle loop entirely. So, once-thru DME synthesis is employed in DMEc leading to much lower DME production than in DMEb but requiring relatively little purchased biomass.

- *Lignin extraction*

In the superstructure (see Figure 21), 25% of lignin extraction takes place as an alternative of black liquor utilization technology. Extracted lignin is used for fuel oil replacement in lime kiln process. Due to the deficit of electricity capacity, some of electricity is purchased to reach power demand of pulp mill (Tomani et al, 2011). Resulting from lignin extraction, benefit of extra pulp production capacity around 10% was included leading to increase of product sale (Benali et al., 2014).

4.3 Optimal process

Superstructure optimization is performed to determine optimal integrated networks for three scenarios; trade-off of pulp pathway between biochemical production and paper production (scenario I), optimal biochemical co-production with pulp for paper production (scenario II) and multiple biochemical products with/without pulp for paper production (scenario III). For each optimal network, results from economic analysis are presented in this section. The optimal network is obtained for each scenario for a plant size of 100,000 tons per year of raw material used. Capital cost is calculated by installed equipment cost that is a function of amount feedstock based on intervals of a processing pathway and considered with 20 years of project life. Raw material and product prices used in the calculations for all scenarios are given in Table 5.

Table 5 Raw material and product price for superstructure optimization

Raw material/Product	Price ($/t)	Reference
Eucalyptus wood	29	Bertran et al. (2017)
Sugarcane bagasse	23	Bertran et al. (2017)
Kraft pulp	544	Manzardo et al. (2014)
Soda pulp	300	Matichon (2008)
Ethanol	769	Bertran et al. (2017)
Lactic acid	2300	Lee (2015)
Succinic acid	3000	Lee (2015)
DME	680	Abdelaziz et al. (2014)
Electricity	40.44	Larson et al. (2006a)

4.3.1 Scenario I: Pulp for biochemical production and paper production as alternatives

For economic decision on selecting one of the possible alternatives of conventional pulp for paper production and production of a biochemical product from unbleached pulp, superstructure optimization is performed to maximize profit (scenario I). Economic results of optimal networks are shown in Table 6. The optimal network is Soda process integrated with succinic acid production and black liquor gasification for DME production that produces 31,227 tons per year of succinic acid and 3,950 tons per year of DME 100,000 tons per year of bagasse. Optimization results for scenario I illustrate that top value-added biochemical products like succinic acid, lactic acid and DME with the existing pulp mill provide higher profit than the traditional pathway, whereas, the one with ethanol product is uneconomical due to its low price. The integrated network with the Soda process obtains higher profit than that with the Kraft process due to lower raw material price and especially utility cost. The optimal integrated biorefinery process has higher profit than the stand-alone Soda process about 60.65 Million US Dollar per year due to integrated high value added biorefinery products of succinic acid and DME. Utility cost is the major operating cost for the integrated biorefinery network that is 77% of total operating cost. The optimal technology pathway of succinic acid purification is electrodialysis with crystallization because sodium hydroxide, neutralizing agent in fermentation, is recycled to save chemical and utility cost, reducing from direct crystallization method about 25% and 17% respectively. Before fermentation, ammonia recycle percolation method and concentrated acid hydrolysis are selected as optimal methods for succinic acid and lactic acid production. As ammonia recycle percolation takes place for pith pretreatment, steam explosion is the suitable method for bark pretreatment. Integrated lactic acid production with Soda process can produce 35,993 tons/year of lactic acid that also provides rather high profit.

From WEASTRA report (Weastra, 2012) succinic acid price would go down to 2,300 \$/ton, reducing about 20%. The profit of the network could be reduced by 32% to 45.83 million \$/year at the reduced price. Due to low ethanol value, ethanol price must increase to 1,011 \$/ton from 769 \$/ton in order to get positive profit. Instead of conventional recovery system, black liquor gasification with DME production is obviously an optimal black liquor utilization for Soda process that can supply energy for pulping process with high value biofuel production. DME synthesis technology with DMEb pathway performing recycled syngas process with GTCC is favorable due to high DME production. Lignin extraction is also a feasible alternative for black liquor utilization due to low capital cost and benefit from extra pulp production. Moreover, development of lignin utilization has widely researched to add value for lignin as biorefinery platform (Ragauskas et al., 2014). Nevertheless, BLGCC with rather high capital cost provides lower profit than Tomlinson boiler with integrated succinic acid production.

In case of integrated biorefinery with the Kraft pulping process shown in Table 7, the optimal pathway is succinic acid production with lignin extraction instead of BLG for DME production. Succinic acid at a rate of 28,863 tons per year can be produced by electrodialysis with crystallization. Lactic acid at a rate of 30,982 tons per year can be produced with the existing Kraft process, offering profitability even the integrated lactic acid network is not the optimal network. Lignin extraction profitably provides extra benefit for the pulp production. Extracted lignin could be applied as biofuel solid instead of purchased fuel oil in lime kiln process. Steam explosion which provides higher conversion of cellulose than other methods is selected for bark pretreatment before concentrated acid hydrolysis. However, the succinic acid production and lignin extraction integrated with Kraft process provides less profit than with Soda process due to less produced succinic acid. Although the integrated BLG/DME is less profitable than the integrated lignin extraction because of higher capital cost, BLG/DME, that produces 7,672 tons of DME per year, is a promising technology for black liquor utilization providing useful biofuel with high profit. In this optimization, the capital cost of Tomlin boiler is not included because Tomlinson boiler is considered as an existing process. If capital cost of Tomlinson boiler is included with lignin extraction that is considered as a new constructed system, capital cost will expand to 1.22 Million $/year. So, BLG/DME is the optimal process replacing implemented lignin extraction with conventional recovery boiler.

Table 6 Economic results of an optimal network and compared networks for scenario I

Profit ($/y)	Product Sale ($/y)	Raw material Cost ($/y)	Chemical Cost ($/y)	Utility Cost ($/y)	Capital Cost ($/y)
Optimal Network					
Soda pulping process with succinic acid production and BLG/DME					
67,684,332	96,367,043	2,300,000	2,482,405	22,211,425	1,688,881
Stand-alone Soda Process					
Soda pulping process with Tomlinson boiler					
7,033,586	10,692,129	2,300,000	819,484	539,059	-
Integrated Biorefinery with Soda Process					
Soda pulping process with succinic acid production and Tomlinson boiler					
66,824,512	93,680,799	2,300,000	2,482,405	22,066,770	7,111
Soda pulping process with succinic acid production and BLGCC					
66,322,321	93,786,010	2,300,000	2,482,405	21,791,922	889,362
Soda pulping process with succinic acid production and lignin extraction					
67,321,204	94,451,556	2,300,000	2,507,880	22,277,679	44,793
Soda pulping process with lactic acid production and BLG/DME					
59,709,719	85,470,839	2,300,000	6,774,506	14,987,535	1,699,079
Soda pulping process with ethanol production and BLG/DME					
-983,275*	6,645,817	2,300,000	2,428,086	1,201,870	1,699,137

*The profit of ethanol production integrated with Soda process will be positive when the ethanol price increase to 1,011 $/ton.

Table 7 Economic results of integrated networks with Kraft process for scenario I

Profit ($/y)	Product Sale ($/y)	Raw material Cost ($/y)	Chemical Cost ($/y)	Utility Cost ($/y)	Capital Cost ($/y)
Optimal Network with Kraft Process					
Kraft pulping process with succinic acid production and lignin extraction					
63,276,163	89,303,657	2,900,000	1,829,471	21,202,444	95,579
Stand-alone Kraft Process					
Kraft pulping process with Tomlinson Boiler					
15,827,635	21,493,521	2,900,000	645,106	2,130,780	-
Integrated Biorefinery with Kraft process					
Kraft pulping process with succinic acid production and BLG/DME					
62,069,266	91,806,240	2,900,000	1,779,995	21,044,624	4,012,355
Kraft pulping process with lactic production and lignin extraction					
51,094,544	73,972,888	2,900,000	6,199,571	13,674,203	104,570
Kraft pulping process with lactic acid production and BLG/DME					
49,887,647	76,475,471	2,900,000	6,150,095	13,516,383	4,021,346

4.3.2 Scenario II: Biochemical co-production with pulp for paper production (20, 50, 80 and 100% of the pulp split for paper production)

Although integrated biorefinery can improve profit of pulp mill, pulp is an important material for paper and packaging production at present. So, scenario II was investigated to optimize the case of biochemical co-production with pulp export for paper production. The amount of pulp split for paper production is specified at different percentages of total unbleached pulp production, i.e. 20, 50, 80 and 100% (Total pulp for paper production). Economic results of optimal networks in different cases are shown in Table 8. The integrated network with the Soda process shows the highest profit for all cases. The Soda process with succinic acid production and black liquor gasification for DME production is an optimal network at 20, 50 and 80% pulp split. Soda pulp and pith are used for succinic acid co-production with pulp for paper production. For the cases of 20 and 50% pulp split, ammonia recycle percolation pretreatment and concentrated acid hydrolysis before the succinic acid process are the optimum routes. But in the case of 80% pulp split, the optimal pretreatment is steam explosion method. Lactic acid process is selected as an optimal integrated process replacing succinic acid for total pulp for paper production (100% of pulp split). Pith is only a feedstock to produce lactic acid by ammonia recycle percolation pretreatment and concentrated acid hydrolysis. DME production is an optimal black liquor utilization for all cases of Soda pulping process. Due to the reduction of biochemical production, the profit of network decreases about 21% with 60% increase of pulp split for paper production but it can respond to the market need of paper production. Considering the Kraft process, implemented succinic acid production and lignin extraction is obviously an optimal biorefinery process. Results of the optimal networks for different cases are presented in Table 9. Integrated biorefinery with the Kraft pulp sale for paper production obtains only 7% lower profit than with the Soda process. Steam explosion is selected for bark pretreatment before succinic acid production in Kraft process. Same as biochemical production in integrated Soda process, concentrated acid method is an appropriate hydrolysis step. The results show that the integrated biorefinery process can improve revenue of pulp mill despite co-production with paper production.

Table 8 Economic results of the optimal networks for scenario II

Product Flow (tons/year)	Profit (M$/y)	Product Sale (M$/y)	Raw material Cost (M$/y)	Chemical Cost (M$/y)	Utility Cost (M$/y)	Capital Cost (M$/y)
20% of pulp for paper production: Soda process with succinic acid production and BLG/DME						
7,128 (Pulp) 26,8577 (SA) 3,950 (DME)	59.78	85.40	2.30	2.30	19.33	1.69
50% of pulp for paper production: Soda process with succinic acid production and BLG/DME						
17,820 (Pulp) 20,022 (SA) 3,950 (DME)	47.26	68.10	2.30	2.04	14.81	1.69
80% of pulp for paper production: Soda process with succinic acid production and BLG/DME						
28,512 (Pulp) 12,824 (SA) 3,950 (DME)	34.47	49.71	2.30	1.71	9.54	1.68
100% of pulp for paper production: Soda process with lactic acid production and BLG/DME						
35,640 (Pulp) 10,388 (LA) 3,950 (DME)	25.14	37.27	2.30	2.68	5.46	1.69

Table 9 Economic results of the optimal networks with Kraft process for scenario II

Product flow (tons/year)	Profit (M$/y)	Product Sale (M$/y)	Raw material Cost (M$/y)	Chemical Cost (M$/y)	Utility Cost (M$/y)	Capital Cost ($/y)
20% of pulp for paper production: Kraft process with succinic acid production and lignin extraction						
7,902 (Pulp) 23,678 (SA)	55.63	78.05	2.90	1.64	17.78	94,547
50% of pulp for paper production: Kraft process with succinic acid production and lignin extraction						
19,755 (Pulp) 15,686 (SA)	43.66	60.52	2.90	1.36	12.50	92,996
80% of pulp for paper production: Kraft process with succinic acid production and lignin extraction						
31,608 (Pulp) 7,694 (SA)	31.69	42.99	2.90	1.08	7.22	91,445
100% of pulp for paper production: Kraft process with succinic acid production and lignin extraction						
39,510 (Pulp) 2,366 (SA)	23.71	31.31	2.90	0.90	3.70	90,411

4.3.3 Scenario III: Multiple biochemical production integrated with pulping process

Production of multiple biochemical products has the flexibility to respond to fluctuating markets. According to scenarios I and II, succinic acid was an optimal product for the integrated biochemical with pulping process. However, current market demand of succinic acid is not high, so it is advantageous if multi-biochemical production is employed such as succinic acid co-production with lactic acid. Lactic acid has also great potential for future bioplastic and polymer besides succinic acid. Scenario III presents optimal pathways and economic data of integrated multiple biochemical production with pulping process along with pulp for paper production. The optimization in scenario III was performed with varying succinic acid productivity by different sugar division to succinic acid process; 30, 50 and 80%. Multi-biochemical co-production with paper production is considered by maintaining the succinic acid productivity to around 10,000 tons per year, based on current succinic acid demand surveyed in Thailand. Table 10 shows product flow and economic results of integrated network with Soda process for scenario III.

Multi-biochemical production integrated with the Soda process gives the highest profit with succinic acid, lactic acid and DME productions. As the results in Table 11, the integrated multi-production with the Kraft process is also a potential network, even if it has lower profit. The results of different succinic acid productivity indicate that the decrease of succinic acid leads to lower profit but only 3-8%. Contrary to utility cost, capital and chemical costs decrease when succinic acid productivity rises. As always, lignin extraction is the optimal process for black liquor utilization in the Kraft process instead of BLG/DME. For the Soda process, ammonia recycle percolation along with concentrated acid hydrolysis is selected but steam explosion is selected as bark pretreatment for the Kraft process. Pulp split for paper production makes profit dwindle to about 10-50% depending on % of pulp split for export to paper production. However, multiple biochemical streams have great potential to improve economic benefit along with supplying pulp according to market need for paper and packaging making process and especially to respond to the volatile market.

Table 10 Economic results of the integrated biochemical networks with Soda process for scenario III

Product flow (t/y)	Profit (M$/y)	Product Sale (M$/y)	Raw material Cost (M$/y)	Chemical Cost (M$/y)	Utility Cost (M$/y)	Capital Cost (M$/y)
Multiple Biochemical Production Integrated in Soda Process						
30% sugar to succinic acid						
9,368 (SA) 25,195 (LA) 3,950 (DME)	61.85	88.74	2.30	5.74	17.15	1.70
50% sugar to succinic acid						
15,613 (SA) 17,997 (LA) 3,950 (DME)	63.28	90.92	2.30	5.04	18.60	1.69
80% sugar to succinic acid						
24,982 (SA) 7,199 (LA) 3,950 (DME)	65.42	94.19	2.30	4.01	20.77	1.69
Multiple Biochemical Production with Soda Pulp Sale						
20% Pulp for paper production						
7,128 (Pulp) 10,144 (SA) 19,141 (LA) 3,950 (DME)	55.04	79.28	2.30	4.84	15.41	1.68
50% Pulp for paper production						
17,820 (Pulp) 10,140 (SA) 11,363 (LA) 3,950 (DME)	44.49	64.61	2.30	3.62	12.52	1.68
80% Pulp for paper production						
28,512 (Pulp) 10,065 (SA) 3,142 (LA) 3,950 (DME)	33.46	48.66	2.30	2.33	8.89	1.68

Table 11 Economic results of the integrated biochemical networks with Kraft process for scenario III

Product flow (tons/year)	Profit (M$/y)	Product Sale (M$/y)	Raw material Cost (M$/y)	Chemical Cost (M$/y)	Utility Cost (M$/y)	Capital Cost (M$/y)
Multiple Biochemical production Integrated in Kraft Process						
30% sugar to succinic acid						
8,659 (SA) 21,687 (LA)	54.49	78.57	2.90	5.15	15.93	0.10
50% sugar to succinic acid						
14,432 (SA) 15,491 (LA)	56.75	81.64	2.90	4.45	17.44	0.10
80% sugar to succinic acid						
23,090 (SA) 6,196 (LA)	60.14	86.24	2.90	3.40	19.70	0.10
Multiple Biochemical production with Kraft pulp sale						
20% Pulp for paper production						
7,902 (Pulp) 10,130 (SA) 14,430 (LA)	49.42	70.59	2.90	3.98	14.20	0.10
50% Pulp for paper production						
19,755 (Pulp) 10,919 (SA) 5,044 (LA)	38.13	57.82	2.90	2.40	11.23	0.09

CHAPTER 5

PROCESS DEVELOPMENT OF SUSTAINABLE BIOREFINERY SYSTEM INTEGRATED INTO THE EXISTING PULPING PROCESS

From the synthesis task, the results of optimal process based on generated superstructure were thoroughly discussed in the previous chapter. The synthesis stage provides the most profitable alternative that is the incorporation of succinic acid (SA) and dimethyl ether (DME) productions into the existing pulp mill. The optimal integrated system is set as base case for process design and innovation. Therefore, this chapter targeted at the process design of this novel biorefinery-integrated pulping process using a simulator to evaluate the performances of the integrated process. Sustainability evaluations including economics, energy and environmental aspects referred to LCA factors (Kalakul et al., 2014; Khoo et al., 2019) were provided also. Based on these evaluations, the bottlenecks for further improvements were identified. The innovations that achieved the improvement targets were generated and subsequently evaluated in the final stage. Accordingly, the application of the three-stage approach for the generations of the biorefinery-integrated pulping process, and the more sustainable alternatives that made use of the versatile biorefinery framework specifically for the improvement of pulping process are revealed that process design, evaluation as well as process improvement in design and innovation stage (Stage II and III) are mainly discussed step by step following the systematic methodology.

5.1 Stage I: Synthesis stage

This stage was performed by superstructure-based process synthesis to modify pulp mill with biorefinery technologies. The methodology is effective to define an optimal integrated process based on the generated superstructure that was designed to implement innovative biorefinery technologies into the existing pulp mill. The optimal integrated network represents the potential integrated biorefinery process to develop as the sustainable process. Process synthesis problem, which involves complex network of integrated alternative technologies needs computer-aided tools for systematical data collection and problem solution. This stage consists of four steps that are briefly reviewed step by step as follows.

5.1.1 Problem definition

To transform the conventional pulp mill by implementing new platforms of biorefinery, biochemical production and black liquor utilization are considered to share raw materials, by-products, utilities and some facilities of the existing pulp mill. Pulp, conventionally exported for paper production, is alternatively considered as feedstock for high value-added biochemical production. Regarding black liquor utilization, the conventional process is Tomlinson boiler with the chemical recovery system. Innovative technologies of black liquor treatment are collected to compare with the conventional process by the superstructure optimization. The goal is to develop the cost-effective biorefinery system with an existing pulp mill based on objective function, performance criteria, process constraints, and technical and economic data. In this work, maximum profit is set as the objective function for superstructure optimization. To systematically collect the data and solve the synthesis problem based on the generated superstructure supporting computer aided tools are needed. The profit of processing routes is calculated from income of product sale and expenditures of raw materials, chemicals, utilities and capital costs.

5.1.2 Data collection – Superstructure generation

The superstructure generation is considered from processing steps and intervals of three main sections; chemical pulping process, cellulose-based biochemical production and black liquor utilization. Kraft pulp mill and Soda pulp mill are selected as receptor pulping process to integrated promising biochemical production via biochemical platform and black liquor utilization technologies via thermochemical platform. The Kraft process utilizes eucalyptus wood chip as a raw material and the Soda process utilizes sugarcane bagasse. Products from pulping process consist of pulp, biomass residue from raw material pretreatment; eucalyptus bark and bagasse pith, and black liquor. Composition of pulping products is different, depending on raw material and pulping technique. Integrated biorefinery technologies are screened by considering market trends, derivatives of products, feasibility and potential developments. Integrated biochemicals considered in this work are (1) succinic acid, (2) lactic acid and (3) ethanol process that have a great potential to be building blocks of biochemical and bioplastic replacing petrochemical route and they can be produced via sugar platform. Pulp is alternatively considered to be hydrolyzed into sugar instead of paper making. While black liquor gasification is a promising thermochemical technology for biofuel production, dimethyl ether synthesis is selected in this case, bioenergy generation via syngas platform. The technologies based on black liquor gasification to compare with conventional process, Tomlinson boiler, include (1) Black liquor gasification combined cycle (BLGCC) for bioenergy production, (2) Black liquor gasification with dimethyl ether production (BLG/DME) for biofuel and energy production. Moreover, technology for (3) lignin extraction from black liquor is included to be an alternative of black liquor utilization in the superstructure. The extracted lignin is employed as biofuel in the lime kiln operation to substitute fuel oil for pulping chemical recovery. Overview of considered processes for superstructure generation is illustrated in Figure 25.

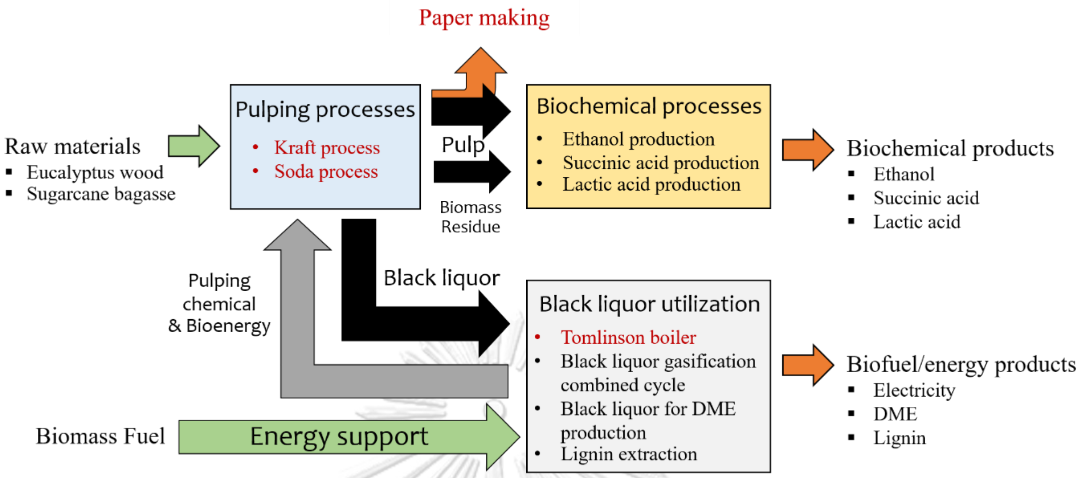


Figure 25 List of considered technologies for superstructure definition

5.1.3 Mathematical model – Problem representation

A set of mathematical models are formulated as a mixed integer (non)linear programming problem or MI(N)LP model representing the synthesis problem (Quaglia et al., 2015). Generic models can represent the superstructure, process constraints, logical constraints and the variable bounds. Super-O is an interface software that can support for collecting the process interval data as component material balance and economic data as raw material, product, chemical and utility price. This in-house software also can formulate and solve the problem of superstructure optimization by interfacing with GAMS solver (Bertran et al., 2017). The maximum profit is set as the objective function as given below.

$$\max Z = C^{P} + C^{R} + C^{U} + \frac{C^{Cap}}{\tau}$$

where C^{P} represents cost-impact vectors of products, C^{R} is of raw materials, C^{U} is of utilities and C^{Cap} represents capital investments.

All of alternative pathways consist of 71 processing intervals, divided into 16 steps of operations and model of superstructure optimization was discussed in Chapter 4. Overview of process intervals and connections is shown in Figure 26.

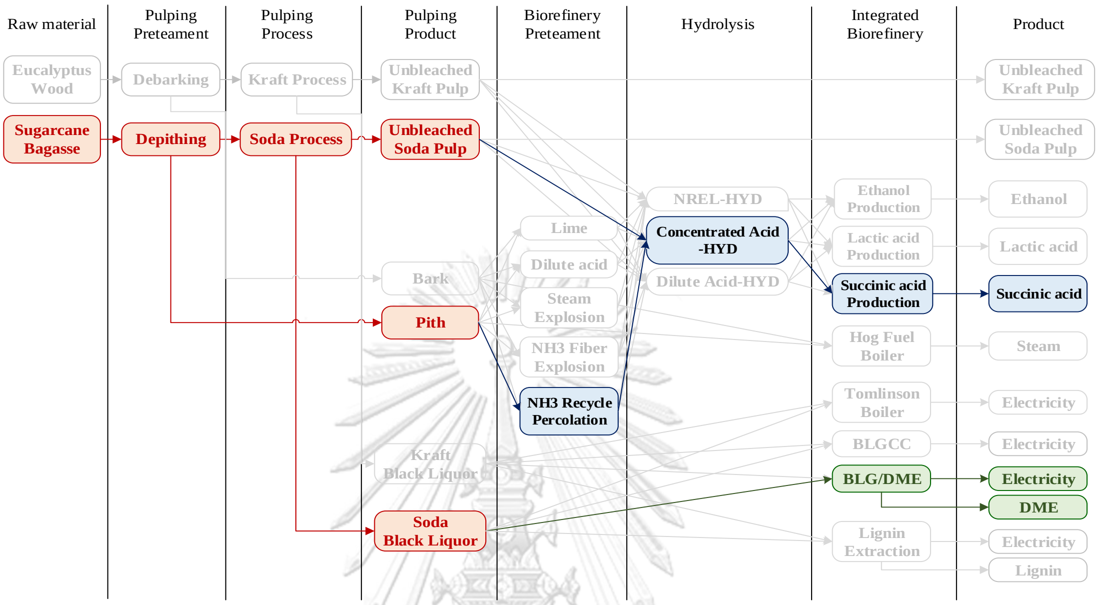


Figure 26 Optimal pathway based on the generated superstructure

5.1.4 <u>Solution of superstructure optimization</u>

The MILP or MINLP models formulated to represent the problem are solved by GAMS (GAMS Development Corporation, 2013) through Super-O interface. Optimal process achieving the objective function that maximize the process profit is defined in three scenarios; (1) single bioproduct from pulp, (2) biochemical co-production with pulp sale and (3) multi-bioproducts. Obviously, Integrated succinic acid and BLG/DME in the Soda pulping process, the colored pathway in Figure 26, is the most promising integrated biorefinery network that can transform low margin of pulp and paper industry to high value of integrated biorefinery network where supplies multiple bioproducts replacing petrochemicals.

5.2 Stage II: Design stage

5.2.1 Base case design

Upon completion of the synthesis stage, the results revealed that the Soda pulping process with the utilization of sugarcane bagasse was the proper receptor for biorefinery-integrated technology. Further, productions of succinic acid (SA) and dimethyl ether (DME) resulted in the maximized profit compared to other alternatives. Thus, the Soda pulping process integrated with the SA and DME productions were considered in the base case as illustrated in Figure 27.

As seen in Figure 27, the network of base case began with the sugarcane bagasse delivered to the Soda pulping process to attain pulps and black liquor. The pulps were utilized in the biochemical process to synthesize SA. The black liquor and pith were processed through the biofuel and energy production unit which produced DME and electricity. Since the required tasks were readily assigned to each block (e.g. gasification, separation, fermentation etc.), proper unit operations must be selected and arranged properly to achieve these tasks. To do so, a rigorous process simulation was employed in order to 1) justify the appropriateness of the selected unit operations, and 2) evaluate the process performances in terms of economic, energy consumption and environmental impact.

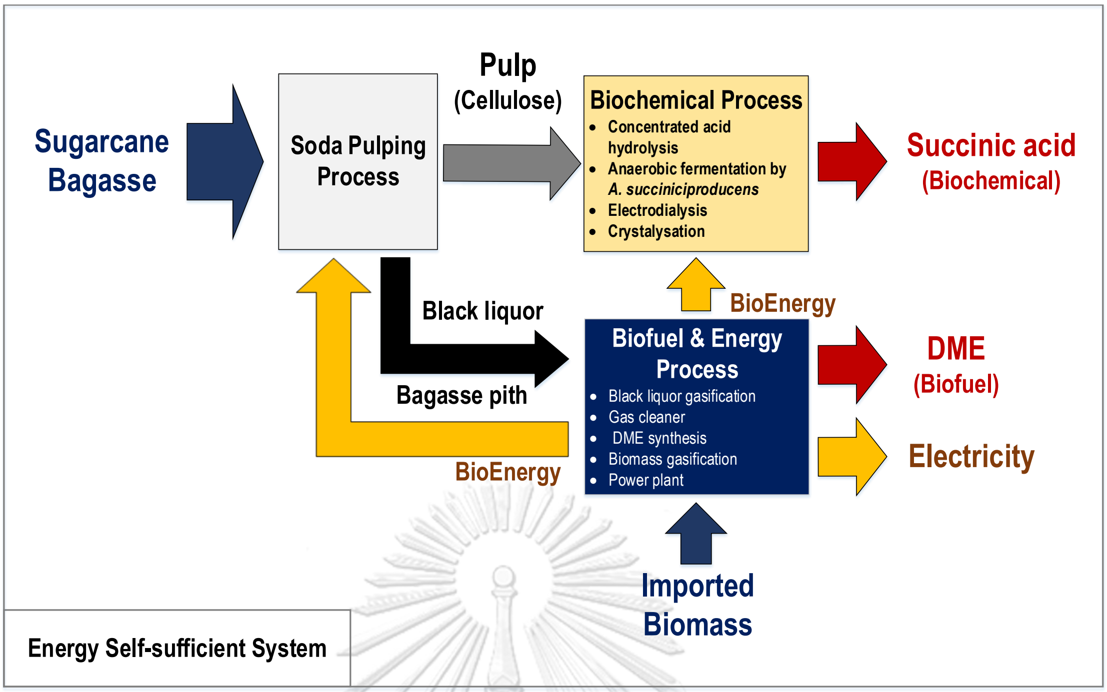


Figure 27 Flowchart of base case design (Soda pulping process integrated with succinic acid and DME production)

5.2.2 Process simulation of base case

Following the base case design, process simulation was conducted using Aspen Plus. Mass and energy balances were conducted in this step which were used for the evaluations of the process performances. In this work, the biorefinery-integrated processes were simulated excluding the pulping process of which information of mass and energy balances were calculated in our previous work (Mongkhonsiri et al., 2018). In the integrated processes, there are five main regions including the black liquor gasification (Figure 29), the gas cleaner (Rectisol technology, Figure 30), the DME synthesis (Figure 31), the pulp hydrolysis (Figure 32), the SA synthesis (Figure 33) and the biomass gasification (Figure 34).

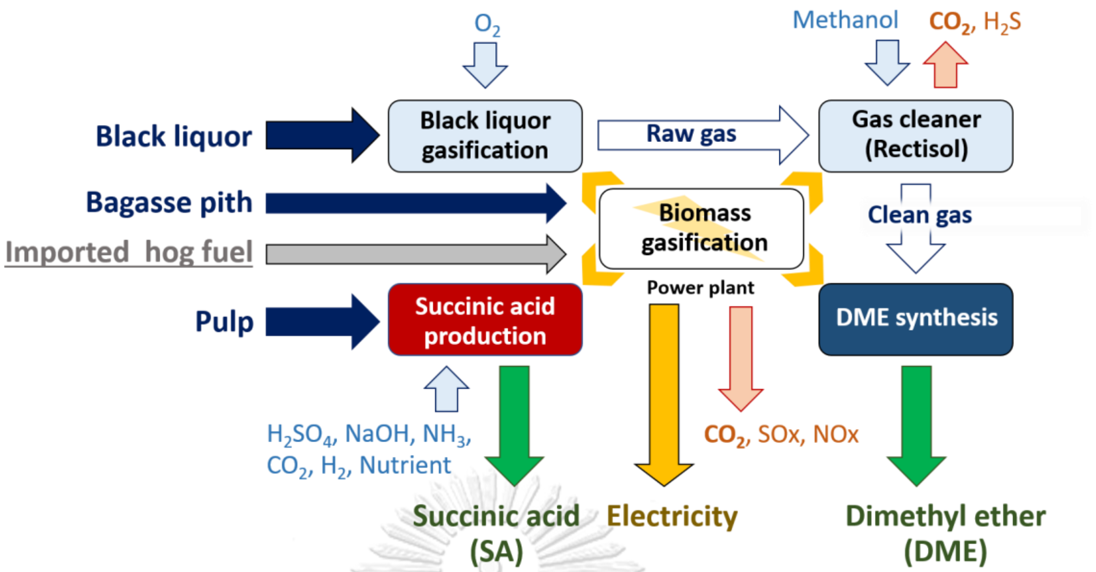


Figure 28 Overview of involved material flow for process simulation

Figure 28 provides the material and production mapping involved in these processes. The quantities of raw material for biorefinery, e.g. pulps, pith and black liquor from the Soda pulp mill were determined based on the feed rate of sugarcane bagasse of 100,000 tons/year which was the current production rate from the pulp mill in Thailand (KTIS 2019). At this bagasse feed rate, pulps were produced and fed to the SA production at 30,700 tons/year contained 71.4%wt glucan, 22.3%wt xylan and 3%wt lignin. The black liquor contained 20% moisture was delivered to the BLG/DME unit at 21,100 tons/year. Biomass residue (bagasse pith) was fed to the biomass gasification process at 22,800 tons/year.

- *Black liquor gasification*

The BLG region produced syngas for DME production. Following the Chemrec technology (Whitty & Nilsson, 2001), the BLG was simulated as a pressurized-oxygen-blown-entrained-flow reactor comprised of two main sections. The upper section was to produce syngas from the gasification of dry solid in the black liquor and oxygen. The products obtained after the gasification contained CO, H_2, CO_2, H_2S, and smelt (sodium-based compounds from pulping chemical). The lower section was the quench section where the gas products and the smelt were cooled by the condensate from the syngas cooler. The inorganic smelt could dissolve in the quench liquid and formed the green liquor which was sent to the lime kiln for the regeneration of pulping chemical. In this study, the black liquor fed to the gasification unit was assumed contained only organic compounds without the inorganic smelt. The operating conditions of the gasifier was at 1000°C and 35 bar. The black liquor was fed with the constituent listed in Table 12.

As provided in Figure 29, the gasifier unit was simulated using three reactors in Aspen Plus including DCOMP (feed decomposition using RYIELD), PYROLYS (Pyrolysis using RGIBBS), COMBUST (Combustion using RGIBBS). Following the literature, the smelt-free syngas left the gasifier at 217°C and 35 bar, and was cooled to about 120°C in the downstream heat exchanger (Lason et al., 2006a). The heat recovered in the cooler could be utilized for the process steam generation. Water contained in the syngas was condensed in the cooler and used as quench liquid for the regeneration of green liquor (not included in this simulation). Chemrec technology produced a minute level of alkali in the syngas which helped protect downstream equipment. Cooled syngas (35°C) was subsequently fed to the gas cleaner to remove acid gases (CO_2 and H_2S) which poisoned the catalyst for DME synthesis. Stream table are shown as Table 13 and the complete stream tables are provided in Appendix D.

Table 12 Composition of feedstocks

	Black liquor	Bagasse pith
Feed flowrate (kg/h)	2530	2730
LHV (MJ/kg)	12.31	12.12
HHV (MJ/kg)	13.87	13.53
	Proximate analysis (%)	
Moisture	20	20
Fixed carbon	28.13	11.88
Volatile matter	40.21	85.2
Ash	31.66	2.92
	Ultimate analysis (%)	
Ash	31.66	2.91
Carbon	36.11	49.2
Hydrogen	4.54	4.69
Nitrogen	1	0.18
Chlorine	0	0
Sulfur	0.45	0.02
Oxygen	26.24	43

Table 13 Stream table from process simulation

	RAWGAS	CLEANGAS	RXIN	RXOUT	DME-PROD	GASTURB	FLUEGAS	PULP	SUGAR	FERMBROTH
Mass Flow (kg/h)	2,180	1,380	5,400	5,400	642	4,590	30,400	3,690	9,000	43,300
Temperature (°C)	35	-50	240	260	44	374	229	25	28	37
Pressure (bar)	33	32	66	62	10	24	1	1	1	1
Mass fraction										
H_2O	0	0	0	0.0039	0	0.1972	0.0683	0.0042	0.5871	0.6465
N_2	0.0133	0.0208	0.1412	0.1412	0	0.0506	0.5943	0	0	0
H_2	0.0411	0.0644	0.0302	0.0141	0	0.0266	0.0001	0	0	0.2487
O_2	0	0	0	0	0	0	0.0252	0	0	0
NO	0	0	0	0	0	0	0.0778	0	0	0
NO_2	0	0	0	0	0	0	0.0721	0	0	0
CO	0.5663	0.8798	0.5704	0.3595	0	0.2249	0.0028	0	0	0
CO_2	0.3514	0.0005	0.1419	0.2460	0.0008	0.4843	0.1488	0	0	0
SO_2	0	0	0	0	0	0	0	0	0	0
SO_3	0	0	0	0	0	0	0	0	0	0
AR	0.0153	0.0233	0.0666	0.0666	0	0.0087	0.0100	0	0	0
H_2S	0.0043	0	0	0	0	0.0001	0	0	0	0
COS	0.0003	0	0	0	0	0	0	0	0	0
CH_4	0.0078	0.0112	0.0455	0.0455	0	0.0076	0.0005	0	0	0
Methanol	0	0	0	0	0	0	0	0	0	0
DME	0	0	0.0042	0.1231	0.9992	0	0	0	0	0
C_2H_2	0	0	0	0	0	0	0	0	0	0
C_2H_4	0	0	0	0	0	0	0	0	0	0
C_2H_6	0	0	0	0	0	0	0	0	0	0

(*Table 13* Cont'd)

	RAWGAS	CLEANGAS	RXIN	RXOUT	DME-PROD	GASTURB	FLUEGAS	PULP	SUGAR	FERMBROTH
H_2SO_4	0	0	0	0	0	0	0	0	0.0117	0
NH_4SO_4	0	0	0	0	0	0	0	0	0	0.0090
DAP	0	0	0	0	0	0	0	0	0	0.0010
NaOH	0	0	0	0	0	0	0	0	0	0.0037
Glucose	0	0	0	0	0	0	0	0	0.3004	0
Galactose	0	0	0	0	0	0	0	0	0.0006	0.0001
Mannose	0	0	0	0	0	0	0	0	0.0002	0.0000
Xylose	0	0	0	0	0	0	0	0	0.0901	0.0102
Arabinos	0	0	0	0	0	0	0	0	0.0067	0.0013
HMF	0	0	0	0	0	0	0	0	0.0004	0.0001
Furfural	0	0	0	0	0	0	0	0	0.0027	0.0006
Acetic acid	0	0	0	0	0	0	0	0	0	0.0131
Lactic acid	0	0	0	0	0	0	0	0	0	0.0027
Succinic acid	0	0	0	0	0	0	0	0	0	0.0622
Acetate	0	0	0	0	0	0	0	0.0024	0	0
Lignin	0	0	0	0	0	0	0	0.0302	0	0
Arabinan	0	0	0	0	0	0	0	0.0165	0	0
Xylan	0	0	0	0	0	0	0	0.2225	0	0
Mannan	0	0	0	0	0	0	0	0.0004	0	0
Galactan	0	0	0	0	0	0	0	0.0020	0	0
Cellulose	0	0	0	0	0	0	0	0.7085	0	0
Formic acid	0	0	0	0	0	0	0	0	0	0.0008
Ash	0	0	0	0	0	0	0	0.0133	0	0

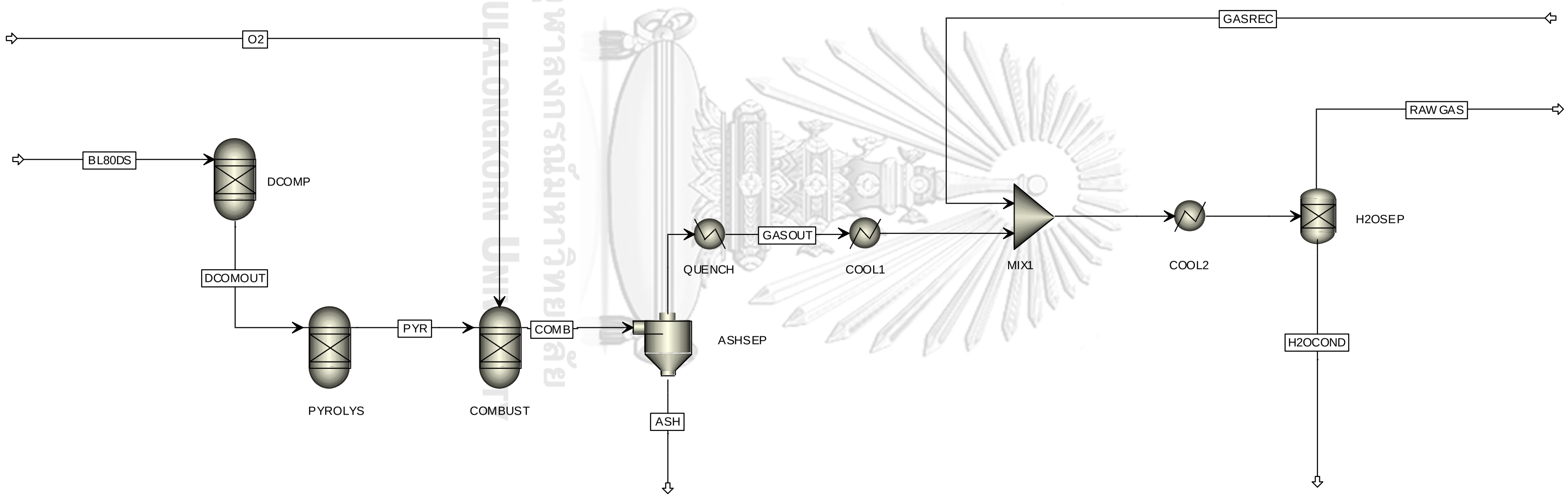


Figure 29 The flowsheet of the simulation for black liquor gasification

- *Gas cleaner*

H_2S and CO_2 contained in the syngas must be removed prior to the DME synthesis. In this case, the concentration of sulfur compounds in the black liquor was low because sodium sulfide (Na_2S) was not utilized in the Soda pulping process. However, H_2S derived from the sulfur compounds must not exceed 0.1 ppm to prevent the catalyst from deactivation during the synthesis of DME (Lason et al., 2006b). CO_2 removal was maximized in this study to maintain the catalyst activity by avoiding the built-up of CO_2 in the recycle loop. Further, the performance of DME production in the reactor was enhanced as a result of the high partial pressures of CO and H_2. Thus, the CO_2 content was monitored at less than 1 mol% in this study.

Rectisol® (Air Products and Chemicals, Inc., 1993) is the most widely used acid gas removal (AGR) technology utilizing methanol as a solvent for physical absorption. The acid gases are removed from the syngas by physical absorption at high pressures without a chemical reaction. Therefore, the solvent can be regenerated easily via indirect heating. The Rectisol technology was adopted in this work to remove both H_2S and CO_2. The process simulation was validated with Lason et al., 2006b. The Rectisol system requires very low temperature of methanol for best performance due to the highly exothermic nature of the CO_2 absorption in methanol. The low operating temperature in the absorber is required to prevent the evaporation of solvent that possibly flows out with the cleaned gas during the absorption process.

Syngas from the gasification of black liquor was cooled to -35 °C and entered at the bottom of the absorber (C1) simulated using RADFRAC in Aspen Plus. The methanol with very low temperature of -50°C (Ranke & Weiss, 1982) was introduced at the top of the column. The cleaned syngas discharged at the top of the absorber was sent to the

DME synthesis with the constituents listed in Table 13. Since the solubility of H_2S in methanol is about five times higher than that of CO_2, H_2S was expected to be captured completely around the bottom section of the column and discharged out of the column through the bottom stream. The side stream above the bottom stream was expected to contain rich CO_2 with nearly no H_2S.

Followed by the absorber C1, three columns including the H_2S Concentrator (C2), the CO_2 Stripper (C3) and the Solvent Regenerator (C4) were simulated using RADFRAC (ProSim, 2015). The H_2S Concentrator (C2) had the stream of almost pure CO_2 discharged at the top of the column and the stream of methanol rich in H_2S discharged at the bottom. In the CO_2 Stripper (C3), CO_2 content was drastically reduced in the methanol stream using nitrogen (N_2) as the stripping agent. In the solvent Regenerator (C4), the methanol residue in the gas phase was condensed, the remained H_2S and CO_2 were discharged at the top of the column while methanol discharged at the bottom was recycled to the absorber (C1). Figure 30 illustrates the process flow diagram of the columns involved in the gas cleaning process.

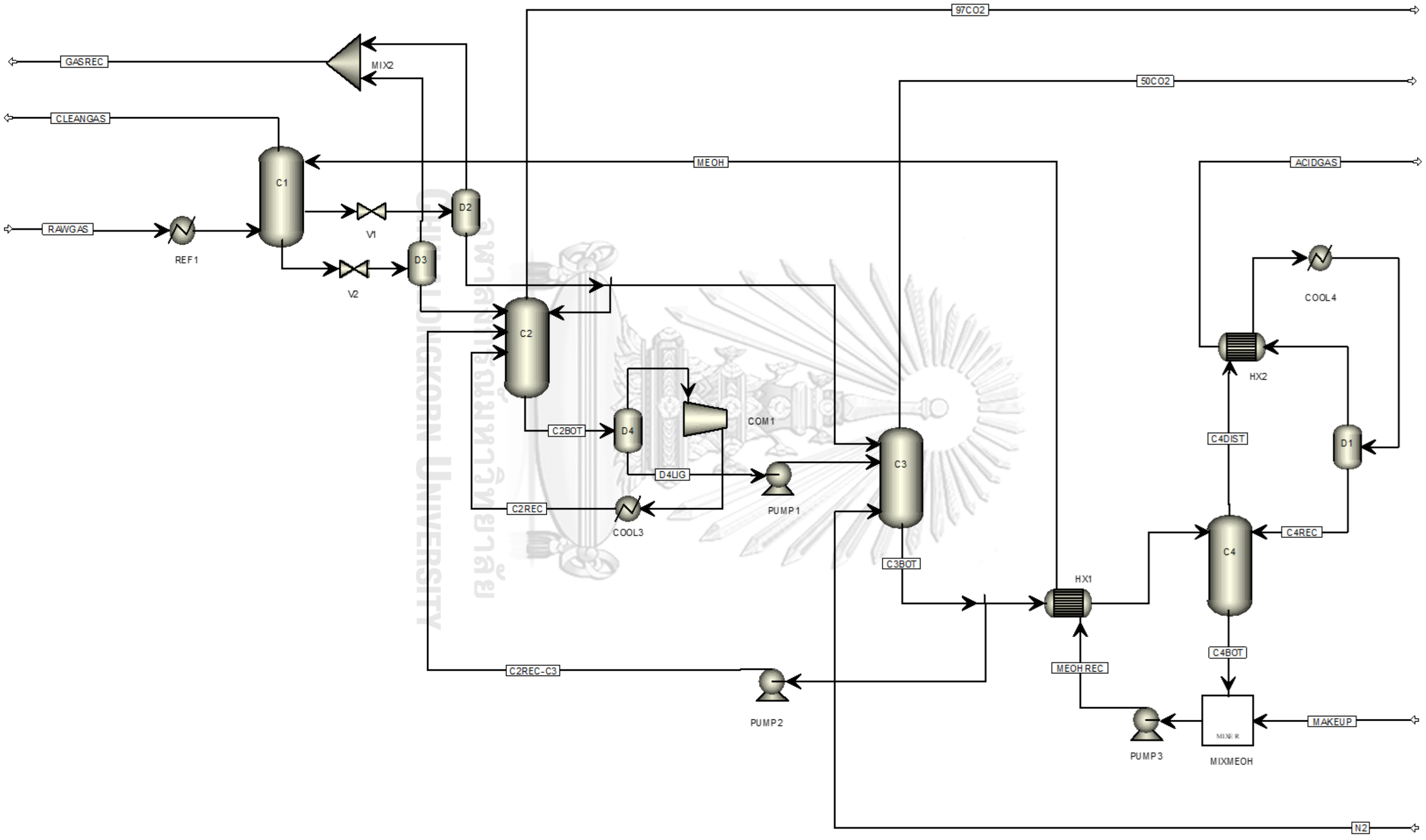


Figure 30 The flowsheet of the simulation for gas cleaner

- *Dimethyl ether synthesis*

The cleaned syngas from the AGR system was heated to 240°C and pressurized to 65.7 bar prior to the delivery of the syngas to the single-step DME synthesis reactor. Inside the reactor, a mix of two catalysts were used: one promoting the synthesis of methanol from syngas and another promoting the dehydration of methanol to DME (Gogate & Vijayaraghavan, 1992). In this work, the liquid-phase DME synthesis reactor (LPDME) was utilized for the DME synthesis simulated using RCSTR with the LHHW kinetic model proposed by Graaf (Beenackers 1996; Ng et al. 1999). Process configuration adapted from Larson & Tingjin, (2003) was simulated as shown in Figure 31.

The reactor operated isothermally at 260°C. Results of inlet and outlet streams are displayed in Table 13. The outlet gases from the reactor were fed into the subsequent separation region where DME product stream was purified to 99.8 wt% by removing methanol, unconverted syngas, and water. Most of unconverted syngas was separated from the product stream by a series of flash tanks. 97% of syngas recovered in the separation region was recycled to the DME synthesis reactor, while the purge gas (3%) was sent to the power plant for energy generation. For product purifications, the first distillation column was used to remove CO2 and other light gases through the distillate stream. The second column was used to separate DME product from methanol/water mixture. Finally, methanol was purified which was recycled to the methanol makeup stream in the gas cleaning region.

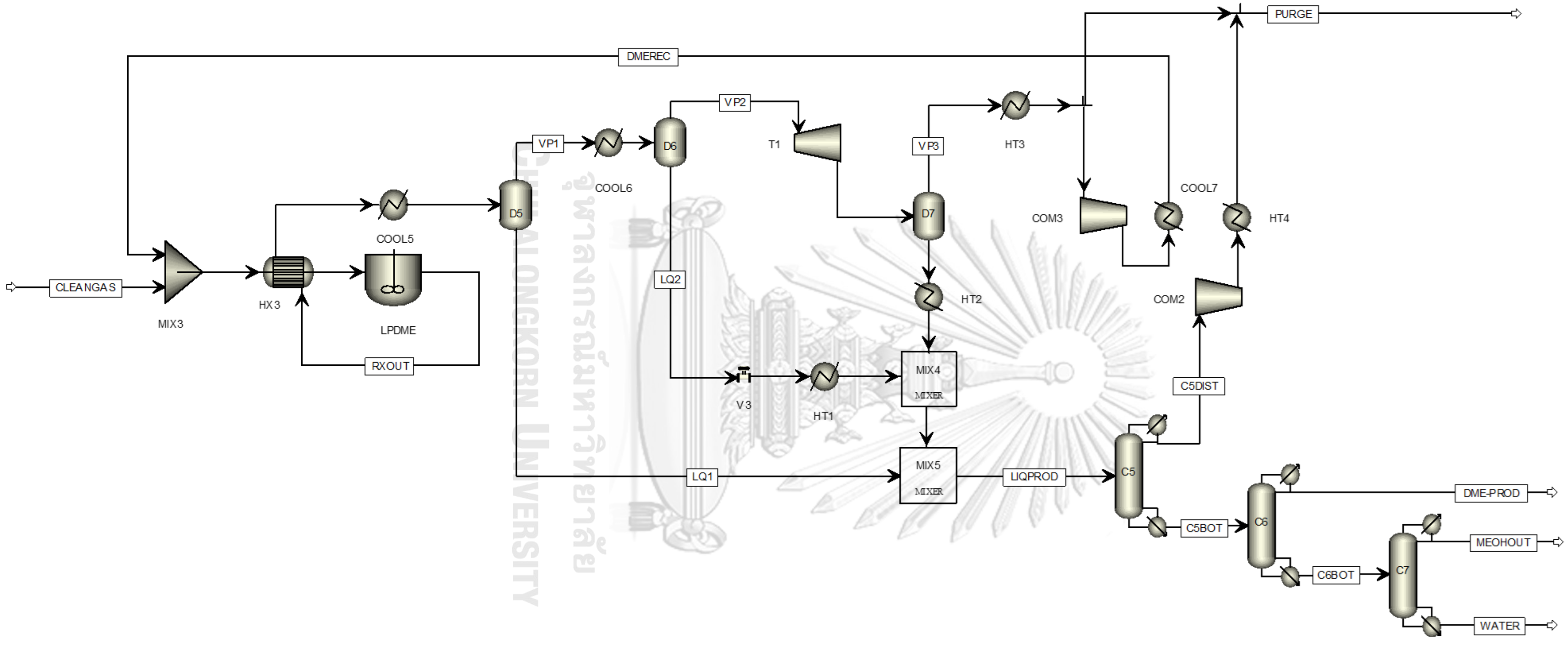


Figure 31 The flowsheet of the simulation for DME synthesis

- *Succinic acid production*

Pulps were utilized as feedstock for SA production in the biorefinery-integrated design. To produce pulps, sugarcane bagasse was processed using pulping chemical (sodium hydroxide in Soda process) to extract lignin and some hemicellulose from cellulose fiber. Contained mainly cellulose, pulps were hydrolyzed subsequently to glucose. SA was produced by the fermentation of sugar and then purified to remove other organic acid by-products. According to our previous work (Mongkhonsiri et al., 2018), the appropriate processing route for the production of SA contained 1) the pulp hydrolysis for the production of sugars using concentrated acid, 2) the fermentation of sugars using A. succiniciproducens strain (Datta, 1992; Lee, 2015) for the production of SA, and 3) the direct crystallization with electrodialysis as the product purification.

The hydrolysis of pulps using concentrated acid was effective in breaking the crystalline structure of cellulose –more than 90% of cellulose was broken at relatively mild temperatures and atmospheric pressure which was possible for enlargement to a commercial scale (Badger, 2002). Two-step hydrolysis of concentrated acid was adopted to hydrolyze pulps to sugar before the fermentation (Wijaya et al., 2014). The flowsheet of hydrolysis process is illustrated in Figure 32. The hydrolysis process was simulated in two reaction steps including the decrystallization and the two-step hydrolysis using concentrated sulfuric acid followed by the product separation. RSTOIC was used to represent the decrystallization and the hydrolysis.

Initially, the raw pulps with composition given in Table 13 and the 75 wt% concentrated acid were mixed in the decrystallization tank at 30°C and atmospheric pressure. In the first hydrolysis tank operated at 30°C, fresh water was fed to dilute the acidic feed to 10 wt% acid in order to minimize the degradation of sugar (Kanchanalai et al., 2016). In the second hydrolysis tank operated at 80°C, the solid product from the first stage was dewatered and soaked in a 30 wt% concentration of sulfuric acid. The dewatered material was dried so that the acid concentration in the material raised to about 70 wt% (Badger, 2002). In this reactor model, the 95% conversion of cellulose to glucose and 88% to xylose were assumed (Kong-Win Chang et al., 2018; Hilpmann et al., 2016). Before the fermentation, the acid/sugar separation and the neutralization process, simulated and represented by T1 and T2 respectively were performed to recycle the acid and deliver the neutralized sugar to the fermenter. The composition of sugar from acid/sugar separation is given in Table 13. To separate sugar from sulfuric acid, this work applied the excellent continuous ion-exclusion chromatography technique (Springfield & Hester, 1999). This technology allowed more than 95% recovery of sugars and 98% acid recovery.

Sugar was equally divided for the seed fermentation and for the direct fermentation to produce SA. The seed fermentation tank (SEEDFERM) contained microorganism, nutrient, fermentation medium and other gases. The fermentation tanks were simulated using RSTOIC with kinetic data from literature (Lee, 2015). Anaerobiospirillum Succiniciproducens was selected to produce SA in this case. After the fermentation, the broth was filtered to remove cells and solid waste. Then, the electrodialysis located before the evaporator and the crystallizer was used to separate sodium hydroxide for reuse as a neutralizing agent in the fermentation step. Simultaneously, succinate salt was converted into SA. Substantial amounts of water and light by-products: e.g. acetate and formate were vaporized using the evaporator. The concentrated succinate was crystallized in the crystallizer operated at 4°C with the pH monitored at 2.0 conditioned by the addition of HCl. At low temperatures, the solubility of SA drops to only 3% compared to other water-miscible by-products such as formic, lactic acid and acetic acid. Finally, the obtained SA crystal was dried to remove moisture and enhance the product purity to 99 wt% (Morales et al., 2016). The process configuration of SA production after the hydrolysis step was displayed by Figure 33.

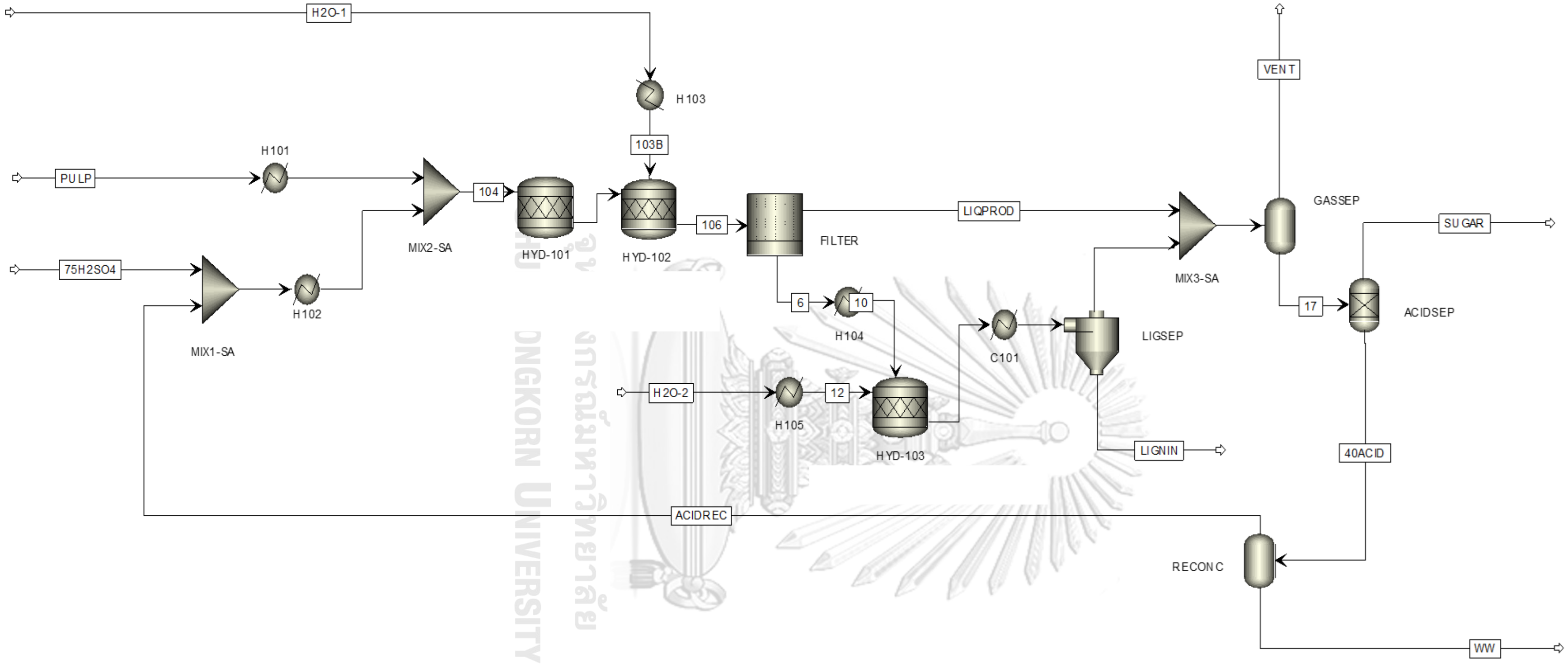


Figure 32 The flowsheet of the simulation for two-step concentrated acid hydrolysis

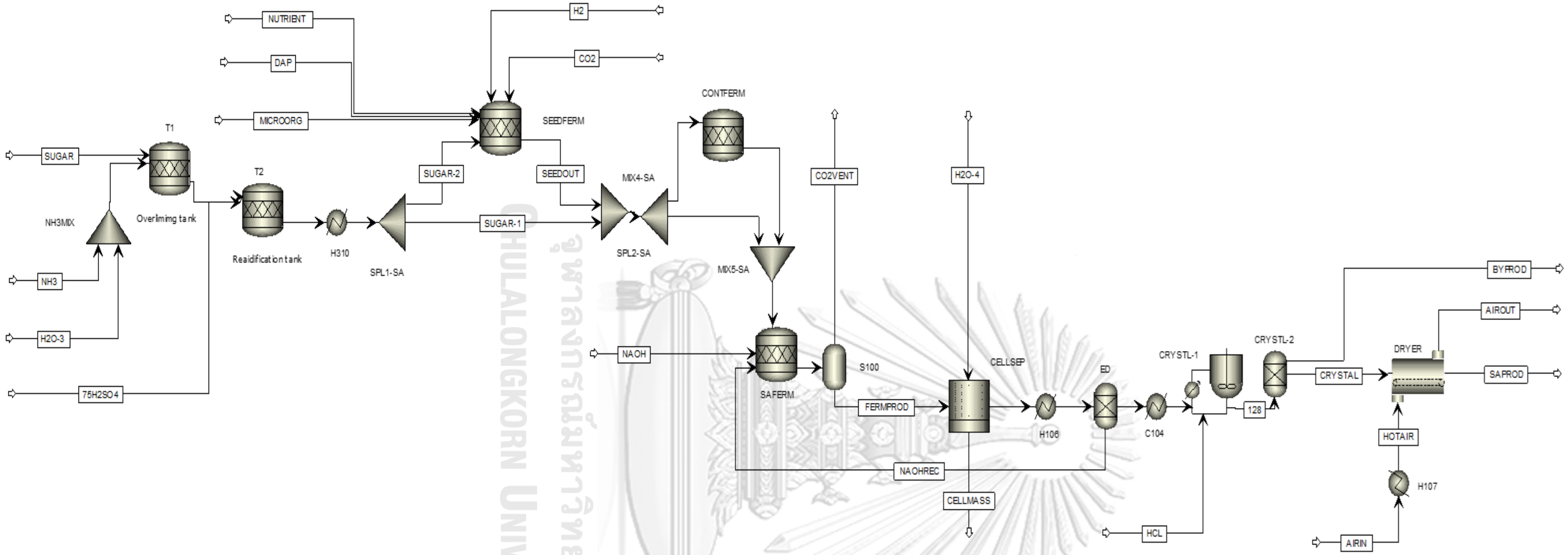


Figure 33 The flowsheet of the simulation for succinic acid production

- *Biomass gasification with power plant*

In the integrated biorefinery designs, pith which was the biomass residue from the bagasse pretreatments (before the pulping step) and imported biomass (purchased as supplementary hog fuel) were processed through the biomass gasification. 20% moisture content contained in biomass was assumed as listed in Table 12 (Mtunzi et al., 2012). Though biomass dryer was not simulated, the energy consumptions for biomass handling and drying were estimated at 5.6 kWh/ton of wet biomass (Consonni & Larson, 1996). Nitrogen obtained from the air separation unit was fed to pressurize the biomass feedstock in the lock hoppers at 36 bar (Blackadder et al., 1994). The pressurized oxygen/steam-blown fluidized-bed gasifier operated at 950 ºC was selected for biomass gasification which was simulated and represented by 4 reactors in Aspen Plus (see Figure 34). DCOMP using RYIELD was initially utilized for the feed decomposition. Then, RSTOIC accounted for the tar formation (Ahmed et al., 2015). After that, volatile compounds were processed by PYRO using RGIBBS.

Char (fixed carbon) was separated and mixed with the mixture of oxygen and steam for gasification in GASIFY (RGIBBS) (Kaushal & Tyagi, 2017). Both product streams were mixed and fed to the catalytic tar cracker (Simell et al., 1996) (simulated by CRACKER using RGIBBS). Steam used as a gasifier agent was provided at a rate of 28% relative to the dry biomass feed rate. The oxygen flow was determined in order to achieve a specified temperature of 950°C at the exit of the gasification system (Larson et al., 2006a). The process simulation of the biomass gasification and the catalytic reforming was validated with a model proposed in Hannula & Kurkela (2012). The temperature of syngas product at the expender exhaust was 375°C with composition listed in Table 13. This syngas was directly utilized as fuel in the gas turbine combined cycle where high-pressure steam was produced for electricity generation. Biomass gasification combined with the power generation system depicted in Figure 34 was designed based on the process configuration from the public report of Lason et al. (2006a).

The gas turbine combustor was installed before the gas turbine system to ensure that any residual tars were converted into light gases. The gas turbine combined cycle was designed to generate electricity for the biorefinery-integrated pulp mill, or for export in case of excess. In this power region design, the gas turbine generator and the heat recovery steam generator (HRSG) operated using the gas-turbine exhaust heat were simulated as provided in Figure 34. Before the HRSG, the duct burner illustrated as BURNER in Figure 34 was employed to provide heat supplementary to the gas-turbine exhaust heat. The duct burner was simulated using HEATER and its outlet temperature of 751°C was assumed. Process details of applied gas turbine were available in the public report of black liquor gasification combined cycle in Kraft pulping process by Larson et al. (2003a).

In this work, electricity produced from the steam turbine (that used high pressure steam from the HRSG) was estimated using the assumed recovery efficiency of 30% relative to the enthalpy change of steam. Essentially, the biomass (bagasse pith and hog fuel) gasification in the power generation region was designed to compensate the parasitic load used in the integrated process. In case of power deficit, electricity could be imported from a grid to meet the power requirement; otherwise, the electricity could be exported to the grid and counted as income.

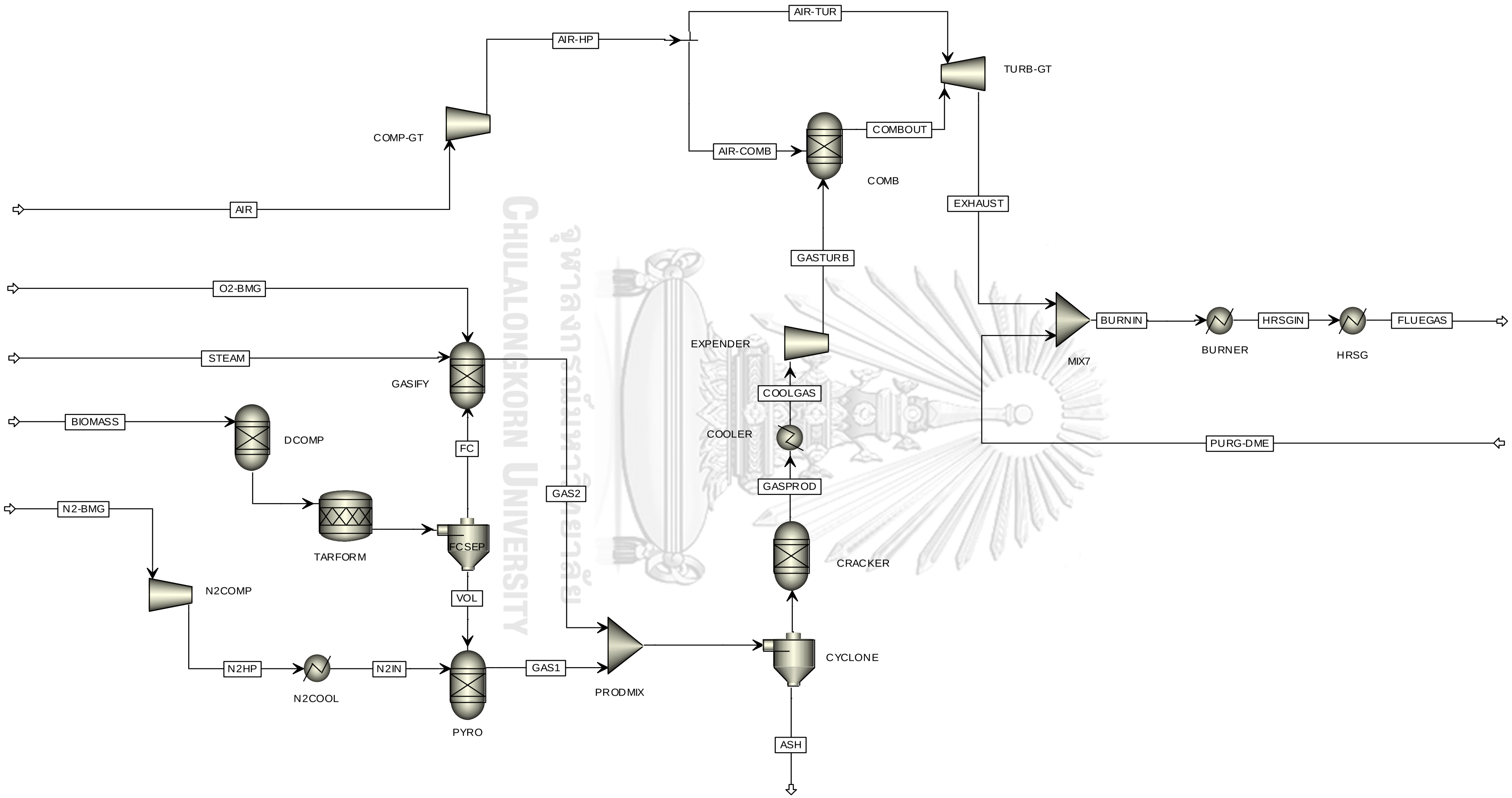


Figure 34 The flowsheet of the simulation for biomass gasification with gas turbine combined cycle

5.2.3 Process evaluation

In this study, three scenarios of biorefinery-integrated processes (assigned as base case) and other two scenarios (Tomlinson and BLGCC that did not implement the biorefinery framework) have been established for comparative purposes. Incorporated to the traditional pulping process, the biorefinery-related scenarios are: the integration of DME production only (Scenario 1), the integration of DME and SA productions with hog fuel as supplement for the power plant (Scenario 2), and the integration of DME and SA productions with the natural gas boost for the power plant (Scenario 3). Process evaluations were determined in terms of the process economic, the power consumption, and the environmental impact. The operation hours per year was assumed at 8,330 hours/year.

For economic assessment in each scenario, the profit of biorefinery-integrated process was estimated based on the product sales, the raw material and chemical costs as well as the power and capital costs (assumed project life of 25 years). Prices of material were collected from the previous publications (Mongkhonsiri et al., 2018, Larson et al., 2006a). Capital costs of the processes excluding the existing pulp mill were calculated based on feedstock flowrate of each region and the capital cost data (e.g. black liquor gasification, DME synthesis, biomass gasification, power plant and air separation plant) from publication (Larson et al., 2006a). The capital cost of SA integrated process was calculated using Aspen Plus. Also, the capital cost of air separation plant (Larson et al., 2006a) that provided O2 and N2 (for the gasification and gas cleaning regions) was also included.

For the estimation of power consumption in each scenario, the power requirement of the integrated process was determined using extracted data from the literature (Larson et al., 2006a) (e.g. pulp mills and air separation plant) and the process simulation (the five regions outlined in Section 5.2.2). The estimated power was compared with the parasitic load obtained from the biomass gasification and power plant region. Please note that the only discrepancy between Scenarios 2 and 3 was the types of supplement –hog fuel was supplied in Scenario 2 whereas natural gas was supplied in Scenario 3. Further, the supplements were required only in these two scenarios which led to the unnecessity import of electricity. However, in Scenario 1, there were no supplements provided to the gasification and power plant region. Thus, extra electricity would be required in these scenarios if the power generated from the gasification of bagasse pith was not sufficient. Conventional Tomlinson boiler and BLGCC that the process performances were calculated by extracted data (Larson et al., 2003) have been illustrated to compare with the scenarios of integrated biorefinery which are considered in this study.

For analysis of the environmental impact in each scenario, the total CO_2 emissions as well as other pollutants such as NO_x, SO_x and PM10 were estimated and assessed.

- *Economic evaluation*

Economic assessments of the biorefinery-integrated (Scenarios 1, 2 and 3) and the conventional (Tomlinson and BLGCC) scenarios were shown in Table 14. As seen in the table, Scenarios 1, 2 and 3 yielded substantially higher profits than those of Tomlinson and BLGCC due to the high values of SA and DME and the excess power sales. Although Scenario 1 had considerably lower profit than Scenarios 2 and 3, the profit was relatively higher in comparison with the Tomlinson and BLGCC. Thus, the incorporation of biorefinery framework to the existing pulp mill was proven enhanced the profitability of integrated processes. However, when compared between Scenarios 2 and 3, the estimated profits were comparable suggesting that other indicators (e.g. power consumption and environmental impact) should be assessed in order to justify the most superior scenario.

Table 14 Process summary of integrated biorefinery scenarios and comparing processes (Tomlinson boiler and BLGCC process)

Info/Process	Unit	/DME/ Scenario 1	DME+SA Scenario 2	DME+SA (Nat.gas) Scenario 3	Tomlinson	BLGCC
Raw material						
Bagasse	ton/y	100,000	100,000	100,000	100,000	100,000
23 $/ton	$/y	2,300,000	2,300,000	2,300,000	2,300,000	2,300,000
Imported biomass	ton/y	-	59,200	-	-	-
23 $/ton	$/y	-	1,362,000	-	-	-
Natural gas boost	ton/y	-	-	9,690	-	643
37 $/ton	$/y	-	-	358,400	-	23,800
Biochemical products						
Pulp sale	ton/y	30,700	-	-	30,700	30,700
300 $/ton	$/y	9,220,000	-	-	9,220,000	9,220,000
DME	ton/y	5,350	5,350	5,350	-	-
680 $/ton	$/y	3,640,000	3,640,000	3,640,000	-	-
SA	ton/y	-	14,700	14,700	-	-
3000 $/ton	$/y	-	43,980,000	43,980,000	-	-
Total biochemical product sale	$/y	12,900,000	47,600,000	47,600,000	9,220,000	9,220,000
Power						
Power sell (+) /buy (-)**	MWh	-3,240	83,100	66,400	-24,100	7,100
*0.14 $/kWh***	$/y	-453,000	11,600,000	9,290,000	-3,370,000	993,000
Capital cost*	$/y	975,000	3,070,000	1,581,000	195,000	344,000
Chemical cost for SA production	$/y	-	954,000	954,000	-	-
Profit	**$/y**	**9,120,000**	**51,600,000**	**51,700,000**	**3,350,000**	**7,540,000**

*Based on non-fuel operating and maintenance costs with 25 years project life excluding pulp mill

**Negative value means power deficit that the purchase of power from other sources is required

- *Power consumption*

The power consumptions estimated for all scenarios are summarized in Table 15. In Tomlinson scenario, the power deficit was observed due to the low efficiency of energy recovery. The BLGCC, on the other hand, could generate the power surplus but it required the natural gas boost indicating the dependency to the fossil fuel. The power consumptions in Scenarios 2 and 3 were considerably higher than other scenarios due to the substantial amount of energy consumed in the SA production (15.8 MW). However, Scenarios 2 and 3 still appeared superior to other scenarios according to the economic point of view.

In comparisons between Scenarios 2 and 3, the natural-gas-boost (Scenario 3) required far less supplement than the imported-hog-fuel (Scenario 2) due to the higher heating value of natural gas relative to hog fuel; 9,860 tons/year of natural gas and 59,200 tons/year hog fuel were estimated. Though required substantially higher supplement, Scenario 2 did not depend on the fossil fuel since the hog fuel was utilized. Further, the power surplus in Scenario 2 was higher when compared to Scenario 3 thanks to the gasification of hog fuel which improved the heating value by transforming hog fuel into syngas. Thus, by considering both economic and power consumption aspects, Scenario 2 was superior to other scenarios.

Table 15 Summary of power consumption of biorefinery-integrated scenarios, Tomlinson boiler and BLGCC processes

Info/Process	Unit	Scenario 1	Scenario 2	Scenario 3	Tomlinson	BLGCC
Raw material						
Bagasse	ton/y	100,000	100,000	100,000	100,000	100,000
Black liquor (80% DS*)	ton/y	21,100	21,100	21,100	21,100	21,100
Pith (80% DS*)	ton/y	22,800	22,800	22,800	22,800	22,800
Pulp	ton/y	30,700	30,700	30,700	30,700	30,700
Imported biomass	ton/y	0	59,200	0	0	0
Natural gas boost	ton/y	0	0	9,680	0	643
Biochemical products						
Pulp sale	ton/y	30,700	0	0	30,700	30,700
DME	ton/y	5,350	5,350	5,350	0	0
SA	ton/y	0	14,700	14,700	0	0
Power						
Power production	MWh	48,500	166,000	135,000	15,300	49,700
Power use (with pulp mill)	MWh	51,700	83,200	68,800	39,300	41,600
Power sell (+) /buy (-)	MWh	-3,240	83,100	66,400	-24,000	7,090

- *Environmental impact*

The net CO_2 and other pollutant emissions (SO_x, NO_x and PM10) were provided in Table 16. For illustration purposes, Figure 35 illustrates comparisons of CO_2 emission/reduction and the net CO_2 associated with each scenario. The biorefinery-integrated processes in scenarios 2 and 3 had higher CO_2 emissions than other scenarios due to the higher power consumptions in the SA productions. However, the processes discharged relatively less SO_x, NO_x and PM10 since the bio-based fuel was used in lieu of the fossil fuel. As observed in Table 16, all scenarios consumed CO_2 within the processes as indicated from the negative values in CO_2 emissions. Though consuming less CO_2 compared to other scenarios, Scenario 2 appeared superior to others providing the highest profitability and the independency on fossil fuel.

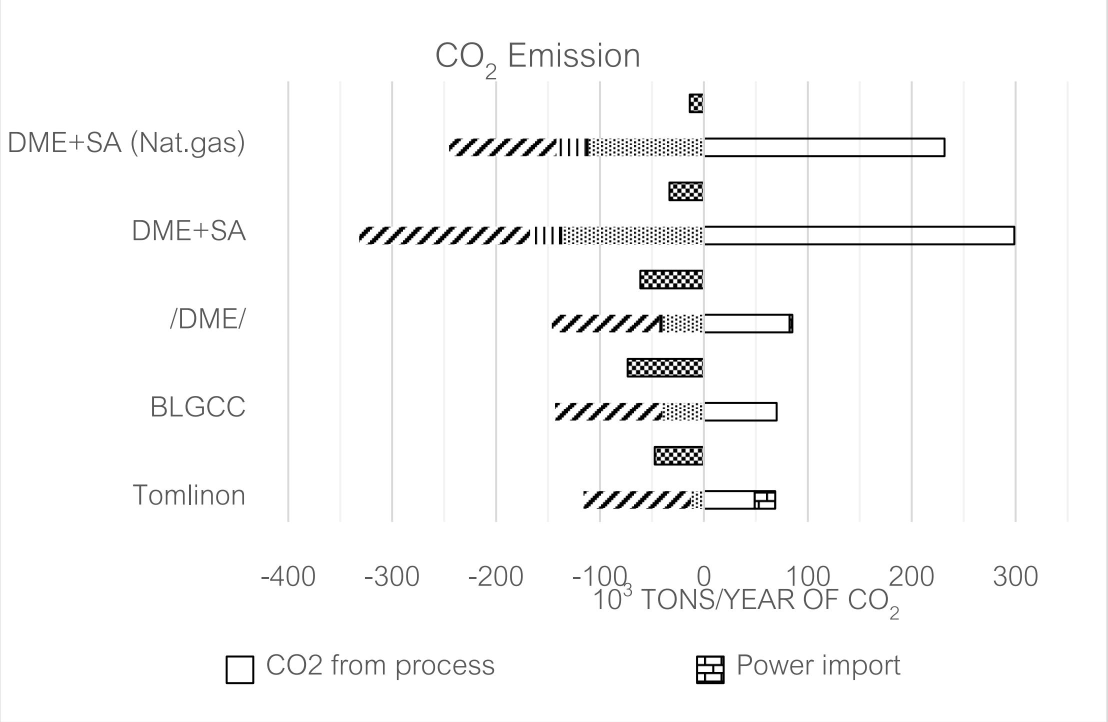


Figure 35 Distributions of CO_2 emission, reduction and net CO_2 associated with each scenario

Table 16 Environmental impacts of biorefinery-integrated scenarios, Tomlinson and BLGCC processes

Info/Process	Unit	Scenario 1	Scenario 2	Scenario 3	Tomlinson	BLGCC
CO_2 Emission						
Process CO_2 emission	ton/y	82,500	299,000	232,000	48,900	70,000
CO_2 from power import (TH-Grid)	ton/y	2,660	-	-	19,700	-
Total CO_2 Emission	ton/y	-	299,000	-	-	-
CO_2 Reduction						
Grid power production replacement (TH-Grid)	ton/y	39,700	136,000	111,000	12,500	40,000
Diesel replacement by DME	ton/y	3,240	3,240	3,240	-	-
Petro-based SA replacement	ton/y	-	27,700	27,700	-	-
Biomass consumption	ton/y	103,000	165,000	103,000	103,000	103,000
Total CO_2 reduction	ton/y	146,000	332,000	245,000	116,000	143,000
Net CO_2 (Emission – Reduction)						
Net CO_2^*	ton/y	-61,300	-33,200	-13,600	-47,300	-73,000
Pollutant Emissions						
Total SO_x Emission	ton/y	29.7	65.9	51.0	96.5	10.3
Net SO_x	ton/y	-185	-561	-468	42.9	-161
Total NO_x Emission	ton/y	22.8	77.2	59.7	55.8	50.9
Net NO_x	ton/y	-101	-96.9	-101	49.3	30.1
Total PM10 Emission	ton/y	4.41	5.77	4.47	32.9	9.3
Net PM10	ton/y	-124	-150	-48.9	19.7	-33.0

5.2.4 Target setting

According to the process evaluations, the designed biorefinery-integrated processes were analyzed to define hotspots and targets based on the bottlenecks of the processes. As seen from the results, the integrated processes with the SA production (Scenarios 2 and 3) caused high CO_2 emissions since the processes required large amounts of energy. Thus, enhancement of CO_2 reduction was set as the improvement target for the integrated SA production scenarios. Though possessing high potential in GHG reductions as observed in Table 16, the integrated DME process without the SA production (Scenario 1) required imported electricity from a grid which still depended on fossil fuel. Thus, an alternative green power was required. For illustrative purposes, the summary of specified targets was depicted in Figure 36.

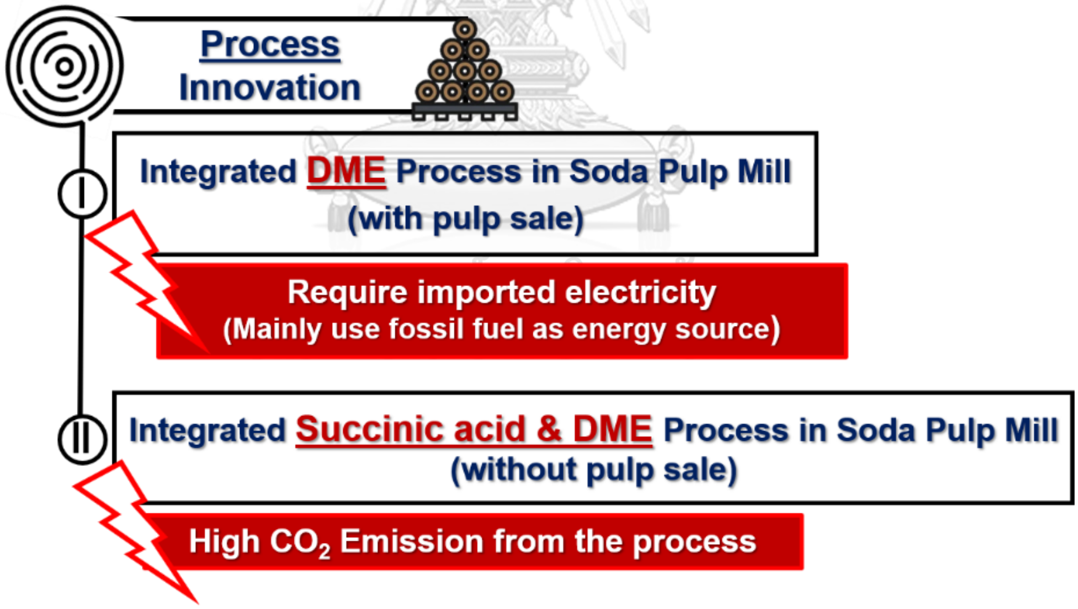


Figure 36 Improvement targets of biorefinery-integrated processes

5.3 Stage III: Innovation stage

Integration of the biorefinery framework into the existing pulp mill was developed to enhance the sustainability of the integrated process. Potentials for the synthesis of new value-added biochemicals and biofuels within the existing infrastructure of pulping process were evaluated to improve the efficiencies of material and energy utilizations, the profitability and environmental impact. As mentioned in Chapter 3, after the performances of base case (the three scenarios) were evaluated, the hot spots and targets were identified. Highlighted in section 5.3 (stage III), the innovations were implemented and reevaluated which were crucial for future recommendations and process improvements.

5.3.1 Alternative generation

Regarding to the established targets for process debottlenecking in stage III, both scenarios of biorefinery-integrated processes could become more sustainable via the applications of innovative green technologies as depicted in Figure 37. For Scenario 1, electricity deficit that required the import of electrical power could be solved using an installation of solar cells. Solar energy has gained a global attention thanks to its low CO_2 emission, low environmental impact and becoming cheaper continuously (IRENA, 2012; IRENA, 2018).

According to the large CO_2 emissions observed in Scenarios 1, 2 and 3, CO_2 was mainly exhausted by the gasification of biomass and power plant. To capture CO_2 in flue gas, the Rectisol process that was readily available in these scenarios could be employed (Xiang et al., 2019). Following the innovative design, CO_2 removed at the absorption column (C2) in the existing Rectisol process was utilized for methanol synthesis via CO_2 hydrogenation (Frauzem, 2017). Methanol produced from CO_2 could be converted to DME at the DME synthesis region. Process flow diagram contained the integration of CO_2 utilization is shown in Figure 38.

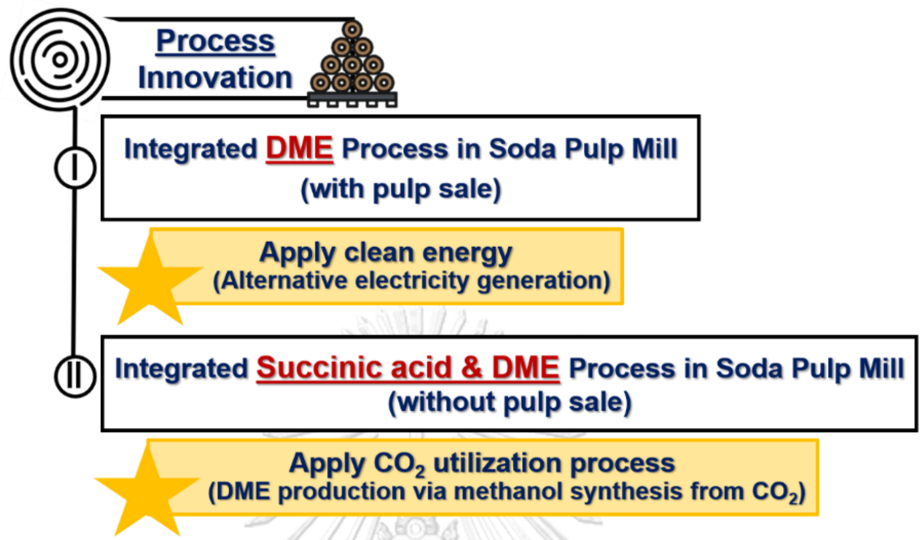


Figure 37 Innovation alternatives of biorefinery-integrated processes

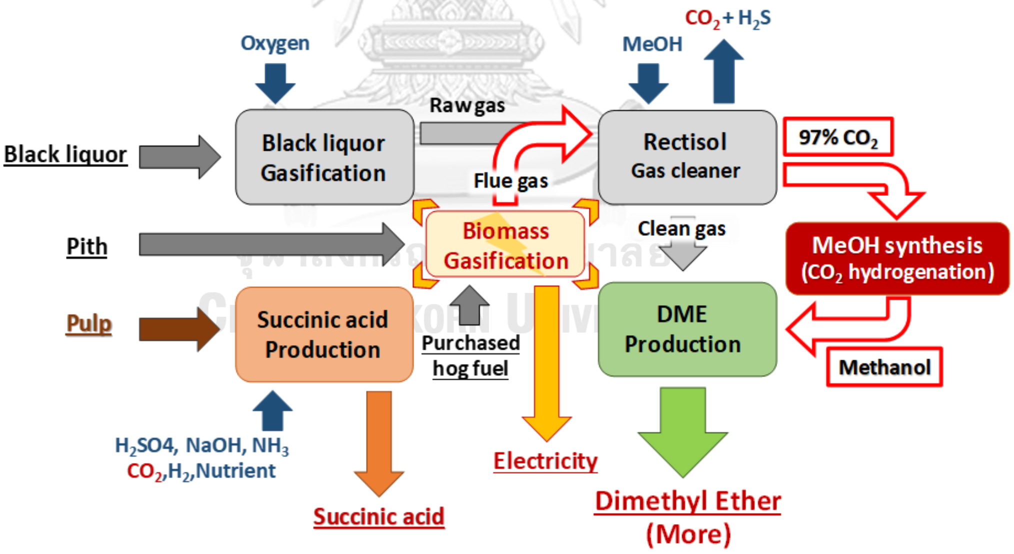


Figure 38 Block diagram of integrated methanol synthesis via CO_2 utilization contained in innovation alternative based on Scenario 2

5.3.2 Alternative evaluation

The generated alternatives based on the improvement targets were evaluated in terms of economic and environmental impacts. As shown in Table 17, utilization of electricity derived from the solar power could reduce the CO_2 emission by 4% (2,530 tons/year) with profit decrease about 2% (194,000 $/year) due to the higher cost of solar energy. Though expensive, the cost of electricity from solar cells had fallen by almost three quarters during 2010 to 2017. Further, by 2020, the solar-photovoltaic system is expected to provide lower cost of energy than the fossil fuel system (IRENA, 2018). Accordingly, the generation of electricity via solar cells appeared plausibly attractive.

To reduce the CO_2 emission, the CO_2 utilization via methanol synthesis was implemented to produce more DME. According to the results, the innovative process achieved the expected target of reducing CO_2 emission; 14,200 tons of CO_2/year was reduced accounting for 42% reduction relative to the base case of integrated SA production (Scenario 2). However, 0.6% profit reduction compared to the base scenario was obtained due to the enlarged chemical, capital and utility costs stem from the addition of methanol plant.

Table 17 Economic evaluations and environmental impacts of the generated alternatives compared with the base case of biorefinery-integrated scenarios based on the improved target

Info/Process		Scenario 1	Scenario 2	DME (SOLAR)	DME+SA (CO_2-MeOH)
Raw material					
Bagasse	ton/y	100,000	100,000	100,000	100,000
23 $/ton	$/y	2,300,000	2,300,000	2,300,000	2,300,000
Imported biomass	ton/y	0	59,200	0	59,200
23 $/ton	$/y	0	1,360,000	0	1,360,000
Biochemical products					
Pulp sale	ton/y	30,700	0	30,700	0
300 $/ton	$/y	9,220,000	0	9,220,000	0
DME	ton/y	5,350	5,350	5,350	31,900
680 $/ton	$/y	3,640,000	3,640,000	3,640,000	21,700,000
SA	ton/y	0	14,700	0	14,700
3000 $/ton	$/y	0	44,400,000	0	44,400,000
Total biochemical product sale	$/y	12,900,000	47,600,000	12,900,000	65,600,000
Power					
Power sell/buy	MWh	-3,240	83,100	-3,240	56,700
0.14 $/kWh	$/y	-453,000	11,600,000	-648,000	7,940,000
Capital cost*	$/y	975,000	3,070,000	195,000	4,340,000
Chemical cost	$/y	-	954,000	-	10,200,000
Extra utility cost	$/y	-	-	-	4,340,000
Profit	$/y	**9,120,000**	**51,600,000**	**8,930,000**	**51,200,000**
CO_2 Emission					
Process CO_2 emission	ton/y	82,500	299,000	82,500	300,000
CO_2 from power import (TH-Grid)	ton/y	2,660	-	130	-
Total CO_2 Emission	ton/y	85,100	299,000	82,600	300,000
CO_2 Reduction					
Grid power replacement (TH-Grid)	ton/y	39,700	136,000	39,700	136,000

CHAPTER 6

NOVEL INTEGRATED BIOREFINERY-KRAFT PULPING NETWORK FOR SUSTAINABLE DEVELOPMENT

This chapter aims to design an integrated biorefinery-Kraft pulping process where the biorefinery concept is combined with pulp and paper transformation. Kraft pulping process is considered as a receptor for the integrated biorefinery technologies, including the gasification-based fuel utilization from black liquor and biomass; the production processes of DME and succinic acid from pulp; and the CO_2 utilization. The integrated biorefinery network is rigorously simulated for process evaluation. The process performance is evaluated in terms of energy, economic and environmental impact for 3 scenarios: (1) an integration of gasification-based DME production without succinic acid production, (2) an integration of gasification-based DME and succinic acid productions, and (3) an integration of innovative CO_2 utilization with DME and succinic acid productions. A comparison of process performances for the three scenarios with the conventional Kraft pulping process with Tomlinson recovery boiler and Black liquor gasification combined cycle (BLGCC) system is presented. Also, the results of process performance are compared with the integrated biorefinery-Soda pulping process from the previous work (Mongkhonsiri et al.,2020) to illustrate the effect of composition of feedstock and pulping products and pulping technology on the intensive performance of the integrated biorefinery network.

6.1 Process description

To integrate a biorefinery with an existing Kraft pulping process, the network is designed to use the extract Kraft pulp as a cellulose source for succinic acid production via acid hydrolysis and sugar fermentation. In the washing stage, white liquor, a solution of mixed sodium sulfate and sodium hydroxide, is used to chemically sever a debarked eucalyptus wood separating lignin and some of hemicelluloses from pulp fiber. After the washing stages, black liquor, a spent cooked-white liquor with organic residues, is sent to an evaporator for concentrated black liquor, then to a chemical recovery system. Conventionally, the Tomlinson recovery boiler is used in the chemical recovery system. In this integrated biorefinery network, it is replaced by BLG for the chemical recovery, converting organic compounds, lignin and hemicellulose, into synthesis gas. Raw syngas is then cleaned by the Rectisol gas cleaner process (Air Products and Chemicals, Inc. 1993), where methanol is used as acid gas absorber agent. A one-step direct DME catalytic reaction is carried out in a suspended-catalyst slurry bed reactor, where a clean syngas is bubbled through a slurry of hot inert oil to produce DME.

Bark is one of by-products that is removed from eucalyptus wood at a raw material pretreatment step before cooking process. In this work, a conventional bark boiler is replaced with a syngas generation by biomass gasification considering bark as a solid precursor coupled with the recovered heat from the biorefinery networks. Gas turbine combined cycle is implemented as power island including a gas turbine generator, a heat recovery steam generator (HRSG), and a steam turbine generator. The syngas, produced from the biomass gasifier, is firstly utilized by the gas turbine to generate electricity. A duct burner is placed between the gas turbine and the HRSG to combust a small amount of syngas enhancing the gas turbine exhaust heat. Then, the gas turbine exhaust heat is used for generating high-pressure steam at the HRSG. The high-pressure steam from HRSG is expanded in steam turbine to obtain utility steam at low and medium pressures. The low and medium pressure steams are supplied to the integrated biorefinery-Kraft pulping network. In the cases the generated electricity and steams do not meet the heat requirement for whole network, imported biomass to gasification island is required for energy supplementary. Electricity requirement is fulfilled by electricity generated from the biomass gasification-based power plant. Depending on the energy generation-consumption of each scenario, excess electricity can be sold. On the other hand, electricity can be purchased from the national energy grid in case of electricity deficit. The integrated biorefinery-Kraft pulping network involves the existing Kraft pulping process, black liquor gasification, Rectisol gas cleaner, DME synthesis, biomass gasification combined power plant, and succinic acid production as illustrated in Figure 39.

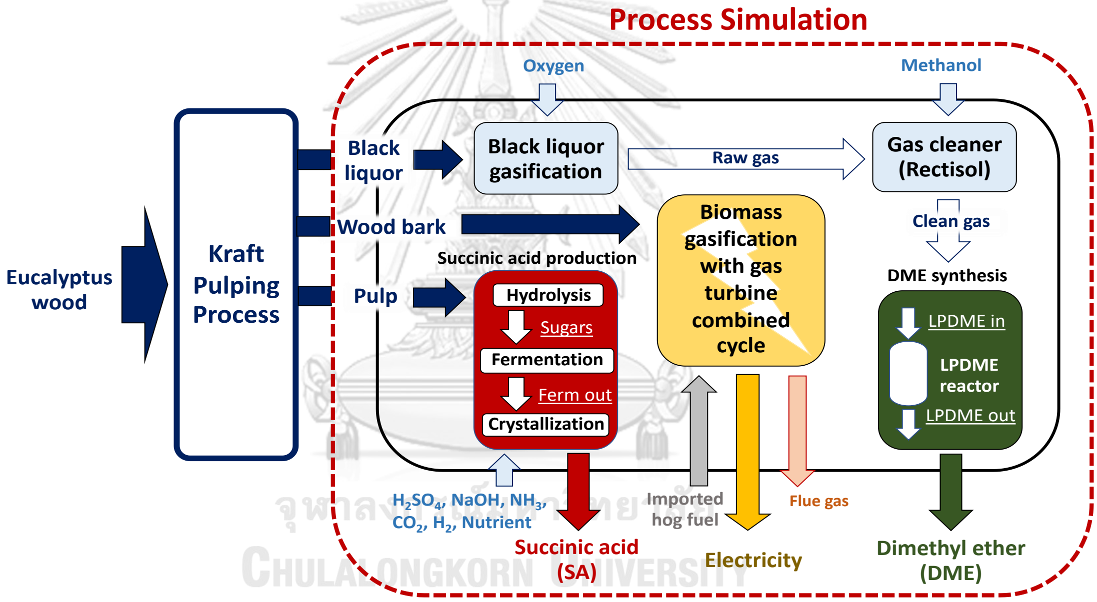


Figure 39 Process flow diagram of integrated biorefinery-Kraft pulping network

6.2 Process simulation

The integrated biorefinery network without Kraft pulping process (biorefinery inside the red line in Figure 39) is rigorously simulated by Aspen Plus to evaluate the performance of the process. These simulated sections include the thermochemical process, converting black liquor to DME; the biomass gasification, generating utility steams and electricity from wood bark; and the biochemical process, producing succinic acid from the unbleached Kraft pulp. The necessary process information and the material and energy balances of the Kraft pulping process is already available from the previous work (Mongkhonsiri et al., 2018). The Kraft pulping process calculation is based on 100 ktons of eucalyptus wood feedstock per year shown in Table 18. From 100 ktons of feedstock, 39.51 ktons of unbleached pulp is manufactured as the main product; 12 ktons of wood bark is acquired and sent to the biomass gasification process; around 40 ktons of black liquor is produced and sent to the BLG then the DME synthesis process. The energy balances take into account the utility steam and electricity required for the Kraft pulping process along with the energy generation in the recovery unit with gasification-based steam and power generator. The Kraft pulping process alone requires 7.15 MW of electricity and 8.8 MWth and 4.2 MWth of low and medium pressure steams respectively. The compositions of the wood bark and the black liquor are classified by proximate and ultimate analyses given in Table 19. The simulation results provide as the stream table in Appendix E.

Table 18 Process information of reference Kraft pulp mill

Mill operating hour	Hour/year	8330
Eucalyptus wood	Tons/year	100,000
Debarked wood chips (20% MC[a])	Tons/year	88,000
Wood bark (50% DS[b])	Tons/year	12,000
Dry bark (80% DS[b])	Tons/year	7,500
Unbleached pulp Yield by wood basis	%Yield	45%
Unbleached Kraft pulp	Tons/year	39,510
Black Liquor Solids Concentration (Organic portion)	% solids	80%
BLS flow rate	Tons/year	38,896
Mill steam use (excluding recovery process)		
Low-pressure (4.8 bars)	MWth	8.8
Medium-pressure (13 bars)	MWth	4.2
Mill electricity use (excluding recovery process)	MWe	7.15

[a] DS denotes dry solid.

[b] MC denotes moisture content.

Table 19 Information of black liquor and wood bark feedstock for gasification process

	Black liquor	Wood bark
Feed flowrate (kg/s)	1.118141	0.215602
LHV (MJ/kg)	12.46	14.5
HHV (MJ/kg)	13.89	16
Proximate analysis		
MOISTURE	20	20
FC	24.59	17.82
VM	35.14	81.38
ASH	40.27	0.8
Ultimate analysis		
ASH	40.27	0.8
CARBON	30.08	49.98
HYDROGEN	3.75	6.12
NITROGEN	0	0.55
CHLORINE	0	0
SULFUR	2.36	0.06
OXYGEN	23.54	42.49

In this study, the black liquor feed was assumed to contain only the organic compounds, which can be burnt into gas products. the composition was classified by proximate and ultimate analyses. The black liquor composition applied in this study was referenced from the work of Consonni et al. (2009) excluding the inorganic elements. Finally, raw gas was cooled to 35°C and consequently sent to the Rectisol gas cleaner process to remove acid gases (CO_2 and H_2S) preventing the catalyst deactivation in DME synthesis unit. Raw gas outlet conditions and compositions from black liquor gasifier were successfully validated by Pilot-Scale Entrained-Flow Black Liquor Gasifier (Jafri et al., 2016) and industrial scale process (Carlsson et al., 2010) as shown in Table 20.

The liquid-phase DME synthesis (LPDME) process was adopted for a one-step DME synthesis. In LPDME, the reaction takes place in a slurry reactor with catalyst suspended in an inert oil while a gas-phase reactant bubbled through. The one-step synthesis involves two intermediate reactions: methanol synthesis from syngas and in-situ methanol dehydration to DME. $CuO/ZnO/Al_2O_3$ catalyst is typically used for the methanol synthesis reaction and acidic α-aluminum is a catalyst for the in-situ dehydration of methanol. Clean syngas from Rectisol AGR process was heated to 240ºC before fed to LPDME reactor at 65.7 bar. The DME synthesis reactor was simulated by as a 260ºC isothermal RCSTR reactor with a LHHW kinetic model. The applied kinetic model based on a methanol synthesis model with an extensive set of accurate kinetic experiments in the CSTR reactor proposed by Graaf & Beenackers (1996) and a model of DME production via methanol dehydration by α-alumina catalyst developed by Ng et al. (1999). The one-step DME process model was originally adopt by Larson & Tingjin, 2003. As shown in Table 21, this simulation was validated by experimental data form Lee et al. (1992). Syngas conversion was deviated about 0.9% from literature; 4.4% for H2 conversion and 1.3% for CO conversion. DME yield has 1.7 % difference.

Table 20 Validation of black liquor gasification process

		Jafri et al., 2016 (OP5)	Carlsson et al., 2010 (October 2008)	This study
Black liquor feed rate	kg/h	1250	1250	4025
O_2/BL	kg/kg	0.285	0.29	0.284
Gasifier pressure	bar	29.9	30	35
Reactor temperature	°C	1004	1020-1080	900-1000
Dry gas composition (% mol)				
H_2		35.4	35.5	36.9
CO		25.0	30.5	28.8
CO_2		35.7	31.0	29.7
CH_4		1.10	1.55	1.66
H_2S		1.70	1.1	1.60
N_2		0.95	-	0.34
COS		-	0.9	0.06

Table 21 Validation of one-step DME synthesis

	Lee et al., 1992		This study	
Catalyst loading (g)	150		150	
	Reactor feed	Reactor product	Reactor feed	Reactor product
Flow rate (mol/h)	2.6786	1.5078	2.6786	1.7069
Component Mole fraction				
Hydrogen	0.3664	0.0802	0.3664	0.1401
CO	0.4750	0.3174	0.4750	0.3264
Methane	0.0840	0.1492	0.0841	0.1319
Carbon dioxide	0.0745	0.2603	0.0745	0.2513
Methanol		0.0263		0.0095
Water		0.0027		0.0032
DME		0.1638		0.1667
Syngas conversion (%)				
Hydrogen		87.7		83.8
CO		62.4		63.2
Total		63.7		64.3

6.3 Process evaluation

Process performance is evaluated in terms of economic aspect, energy consumption and environmental impact based on rigorous information obtained from the simulated process. Operating hour is assumed to be 8,330 hours per year and the eucalyptus feed rate is 100 ktons per year. The indicator for an economic efficiency is an annual profit estimated from operating and capital costs. The operating costs involve the cost of fed eucalyptus wood, the imported biomass fuel, natural gas or electricity, and the added chemical. The price of feedstock and product are given in Table 22. The capital cost includes only the integrated biorefinery network without the facility of existing Kraft pulping process. The capital cost for the biomass gasification process is estimated based on the simulated data taken from Larson et al. (2006a). The capital cost of the succinic acid production process is rigorously calculated based on simulated process. The energy balance for the heat and electricity consumptions and productions are obtained from the rigorous simulated process together with the calculated data reported by Larson et al. (2006a). The environment impacts are evaluated by net emissions of pollutants: CO_2, SO_x, NO_x and PM10. Following equation (1), the net gas emissions considers the gas emission from the processes estimated by emission factor given in Larson et al. (2006c) and the potential of gas reduction

$$Net\ gas\ = \sum Gas_{Emission} - \sum Gas_{Reduction} \tag{1}$$

Net gas refers to net gas emission acquired by difference of Total gas emission ($Gas_{Emission}$) and gas reduction ($Gas_{Reduction}$) by the biomass utilization, the fossil-based products replacement; the diesel replacement by DME, the petroleum-based succinic acid and the fossil-based electricity generation based on the national grid of Thailand.

Table 22 Price of raw material, products and electricity price for economic evaluation

	Price	Reference
Eucalyptus wood	29 \$/t	Bertran et al. (2017)
Kraft pulp	544 \$/t	Manzardo et al. (2014)
Succinic acid	3000 \$/t	Lee (2015)
DME	680 \$/t	Abdelaziz et al. (2014)
Electricity	0.1 \$/kWh	MEA Thailand (2020)
Biomass fuel	23 \$/t	Mongkhonsiri et al., (2018)
Natural gas	2.03 \$/MMBtu	EIA (2020)
75% H_2SO_4	27 \$/t	Database
H_2O	0.22 \$/t	Database
NH3	420 \$/t	Database
NaOH	400 \$/t	Database
HCl	90 \$/t	Database
Diammonium phosphate (Fermentation medium)	156 \$/t	Database
Corn steep liquor (Nutient)	177 \$/t	Database
Microorganism	25 \$/t	Database

Process evaluations were performed in three different scenarios.

Scenario I: *Integration of the gasification-based DME production without succinic acid production*. This scenario considers only integrating the BLG, the DME production and the biomass fuel utilization. Since the succinic acid production is excluded; the unbleached pulp product is conventionally sold for paper making.

Scenario II: *Integration of gasification-based DME and succinic acid productions*. This scenario includes the succinic acid production from the unbleached pulp, together with the integrated network from scenario I. The energy consumption of the succinic acid production process is added to the total energy requirement.

Scenario III: *Integration of the innovative* CO_2 *utilization* with DME and succinic acid production. This scenario includes the CO_2 utilization into the integrated network from scenario II. Because energy consumption increased with the integrated succinic acid production in Scenario II; the CO_2 emission from biomass gasification and power plant is also increased. This innovative scenario is designed to utilize the CO_2 to produce more DME. This scenario is integrating the carbon capture process report by Hedstrom (2014) to the integrated network in scenario II. Before CO_2 is exhausted, the CO_2 contained in power plant-generated flue gas is captured by the existing Rectisol process without the additional installation cost. The biomass gasification with CO_2 capture design is investigated in an oxy-fuel atmosphere instead of air (Xiang et al., 2019). Following the innovative design, CO_2 is removed at the H_2S concentration column in the existing Rectisol process. 98% of the recovered CO_2 is utilized for the methanol synthesis by the integrated CO_2 hydrogenation process with hydrogen. The performance of the methanol synthesis process has already been evaluated in term of economic and environmental impacts by Frauzem (2017). The produced methanol is then supplied to the DME synthesis process. The process diagram of the innovative CO_2 utilization – methanol synthesis is illustrated in Figure 40. 33.9 ktons of methanol is estimated to be produced per year based on 50% yield of CO_2 feed rate. Hence, 30 ktons more per year of DME is acquired by the additional methanol feed to the DME production process.

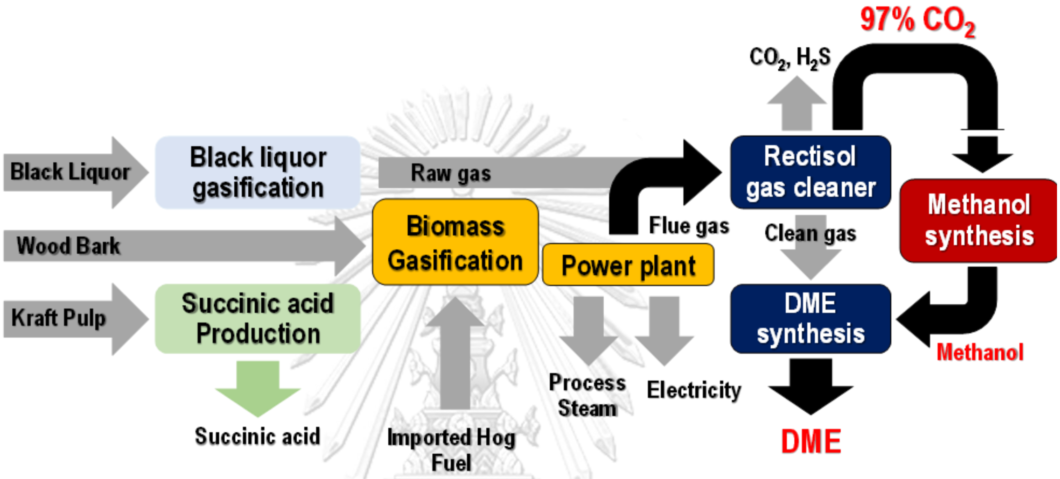


Figure 40 Process innovation for CO_2 utilization by integrated methanol synthesis

6.4 Results and discussion

Results of the mass and energy balances were shown in Table 23. The conventional Tomlinson boiler and BLGCC information acquired from the work of Larson et al. (2003) were given to illustrate the comparison with the studied scenarios. Also, the result of the Soda pulping process integrated biorefinery from the previous work (Mongkhonsiri et al., 2020) was given for comparison with the same implemented scenarios and discussed in section 6.4.4.

6.4.1 Energy performance

Beside the integrated biorefinery-Kraft pulping network the energy consumptions from an air separation plant, a steam cycle auxiliary and a biomass handling and drying process are included. The required utility steams for the whole integrated biorefinery-Kraft pulping network can be met by the generated steams from biomass gasification combined cycle.

The results of power generations and consumptions in different scenarios are displayed in Table 23. In all scenarios, the additional purchasing of the biomass for the energy generation is required albeit different amount based on the heat – energy deficits. In the scenario I, the integrated network with gasification-based DME production consumes about 60 ktons per year less of the imported biomass than other scenarios because the succinic acid production process demands 16 MW of heat more. Consequently in the scenario II, the integrated DME and succinic acid productions network generates 97,000 MWh more of electricity; meanwhile in scenario III, the additional integration of the CO_2 utilization network consumes 143,000 MWh of electricity with same amount of electricity generated in scenario II due to the increased energy demand of the Rectisol process and the DME synthesis. Therefore, the electricity exported is reduced 40% compare to scenario II. Comparing to the conventional Tomlinson boiler or the BLGCC that need to import 40,600 MWh and 1,200 MWh of the electricity from the national grid respectively; all scenarios of the integrated biorefinery-Kraft pulping network can export the cleaner bio-based electricity back to the national grid which will affect both the operating cost and the pollution emissions.

Table 23 Material flow and power balance of integrated biorefinery scenarios comparing to conventional Tomlinson boiler and BLGCC system.

Info/Process	Unit	Scenario I	Scenario II	Scenario III	Tomlinson	BLGCC
Feedstocks						
Eucalyptus wood	ton/y	100,000	100,000	100,000	100,000	100,000
Black liquor (80% DS[a])	ton/y	38,900	38,900	38,900	38,900	38,900
Bark (80% DS[a])	ton/y	7,500	7,500	7,500	7,500	7,500
Pulp	ton/y	39,500	39,500	39,500	39,500	39,500
Imported biomass	ton/y	42,500	102,500	102,500	-	-
Natural gas boost	MMBtu/y	-	-	-	-	15,100
Biochemical products						
Pulp sale	ton/y	39,510	-	-	39,510	39,510
DME	ton/y	5,920	5,920	30,000	-	-
Succinic acid	ton/y	-	17,800	17,800	-	-
Power						
Power production	MWh	88,000	185,000	185,000	20,600	63,800
Power use[b]						
Pulp mill	MWh	59,600	59,600	59,600	59,600	59,600
Air separation plant	MWh	11,700	21,400	21,400	-	3,700
Black liquor Gasification	MWh	19.40	19.40	19.40	-	19.40
Rectisol AGC & Sulfer recovery	MWh	1,740	1,740	7,690	-	-
DME synthesis	MWh	4,870	4,870	26,200	-	-
BMG/Bark boiler[c]	MWh	2,100	4,620	4,620	403	483
Succinic acid	MWh	-	18,200	18,200	-	-
Steam cycle auxiliary	MWh	1,270	2,930	2,930	1,210	1,210
Biomass handling and drying	MWh	917	2,020	2,020	-	-
Total power consumption	MWh	82,200	115,000	143,000	61,200	65,000
Power export (+)/import (-)[d]	MWh	5,800	70,000	42,000	-40,600	-1,200

[a] DS denotes dry solid.

[d] In scenario III, power use was considered for larger Rectisol gas cleaner and DME synthesis process but not included for power use of integrated methanol synthesis process that was calculated as extra utility cost in economic evaluation.

[c] Bark boiler was considered in case of Conventional Kraft mill with Tomlinson boiler and Black liquor gasification combine cycle.

[d] Negative value means power deficit that the purchase of power from other sources is required.

6.4.2 Economic evaluation

The profits of integrated biorefinery-Kraft pulping network are evaluated with the assumed 25 years of project lifetime and compared to the conventional Tomlinson boiler and the BLGCC process. The operating costs comprise the raw material and chemical costs and the power import; while the capital cost excludes the equipment and installation costs of the existing Kraft pulping process.

The results of the economic assessment are reported in Table 24. The integration of DME and succinic acid production (scenario II) and the innovative CO_2 utilization with DME and succinic acid productions (scenario III) do highly promote profitability of the existing Kraft pulping process up to 55 million US dollar per year due to the higher succinic acid price overcoming the low unbleached pulp price; moreover, the excess electricity sold to the national grid also increases the benefit of the integrated networks. The CO_2 utilization applied in scenario III increases profit around a million US dollar per year over scenario II due to the additional DME production from CO_2; however, it demands extra operating cost of the larger Rectisol gas cleaner unit for CO_2 capture, additional operating cost for the DME production and extra expenditure for the methanol synthesis. On the other hand, scenario II offers the highest income from electricity export about 7 million US dollar per year compare to 4.2 million US dollar per year from scenario III with the same cost of biomass fuel. Although scenario I yields half the profit of the other scenarios, it still improves the profit over the conventional Tomlinson boiler and BLGCC processes. The conventional Tomlinson boiler is estimated to gain around 14 million US dollar per year of profit, whereas the BLGCC improves the profit to around 18 million US dollar per year; the scenario I enhances the profit further to around 20 million US dollar per year.

The biorefinery-Kraft pulping networks in scenarios I, II and III promote the biochemicals income compare to the conventional Kraft pulping process by 6 , 36, 96 Million US dollar respectively. Moreover, the excess power available in all integrated network scenarios provide additional income from electricity sold, as well as reduce the petroleum-based dependency.

Table 24 Economic evaluation of integrated biorefinery scenarios

Info/Process	Unit	Scenario I	Scenario II	Scenario III	Tomlinson	BLGCC
Raw material cost						
Eucalyptus wood	ton/y	100,000	100,000	100,000	100,000	100,000
29 $/ton	$/y	2,900,000	2,900,000	2,900,000	2,900,000	2,900,000
Purchased biomass	ton/y	42,500	102,500	102,500	-	-
23 $/ton	$/y	977,500	2,357,500	2,357,500	-	-
Natural gas boost	MMBtu/y	-	-	-	-	15,100
2.03 $/MMBtu	$/y	-	-	-	-	30,653
Total raw material cost	$/y	3,877,500	5,257,500	5,257,500	2,900,000	2,930,653
Biochemical products sale						
Pulp sale	ton/y	39,510	-	-	39,510	39,510
544 $/ton	$/y	21,493,440	-	-	21,493,440	21,493,440
DME	ton/y	5,920	5,920	30,000	-	-
680 $/ton	$/y	4,025,600	4,025,600	20,400,000	-	-
Succinic acid	ton/y	-	17,800	17,800	-	-
3000 $/ton	$/y	-	53,400,000	53,400,000	-	-
Total bio-products income	$/y	25,519,040	57,425,600	73,800,000	21,493,440	21,493,440
Power income/cost						
Power production	MWh	88,000	185,000	185,000	20,600	63,800
Power use	MWh	82,200	115,000	143,000	61,200	65,000

Power export (+)/import (-)[a]	MWh	5,800	70,000	42,000	-40,600	-1,200
0.1 $/kWh	$/y	580,000	7,000,000	4,200,000	-4,060,000	-120,000
Capital cost	$/y	908,000	1,950,000	2,340,000	154,676	272,797
Non-fuel operating cost for gasification-based units	$/y	908,000	1,950,000	2,340,000	154,676	272,797
Chemical cost for SA process and methanol synthesis	$/y	-	1,200,000	9,170,000	-	-
Utility cost for methanol synthesis	$/y	-	-	3,760,000	-	-
Profit	**$/y**	**20,405,540**	**54,068,100**	**55,132,500**	**14,223,440**	**17,896,787**

[a] Negative value means power deficit that the purchase of power from other sources is required

6.4.3 Environmental impact

The environmental impacts of the integrated biorefinery system were indicated by the net pollutants: CO_2, SO_x, NO_x and PM10 emissions. The results of emission and the potential reduction of pollutants were shown in Table 25. The pollutants emissions were mainly resulted from energy consumptions and the switch to the greener bioenergy source in the gasification-based biorefinery. The amount of pollutants emissions was calculated based on the syngas produced by biomass fuel in the integrated biorefinery scenarios or the black liquor utilization in cases of the conventional Tomlinson boiler and BLGCC with referenced emission factors (Larson et al., 2006b). The pollutants are mainly emitted as a flue gas from the power plant where the supplied heat and electricity are generated for whole system including Kraft pulp mill. Additionally, there are an additional 0.15 tons CO_2eq emission per tons succinic acid from the integrated succinic acid process (Smidt et al., 2016) and an additional 0.2 tons CO_2eq emission per tons methanol synthesized via CO_2 hydrogenation. Regarding to the CO_2 and pollutants reduction, the potential of reduction was defined by the conventional fossil-based products replacement that involve the bio-based electricity, bio-DME and bio-succinic acid.

The integrated biorefinery with succinic acid production processes (scenario II and III) have around 2 times higher CO_2 and other pollutants emission comparing to the scenario without succinic acid because it requires higher energy for the integrated succinic acid production. Scenario III with the implement CO_2 utilization configuration diminishes the CO_2 emission 47,000 and 65,000 tons per year comparing to scenario I and II, respectively. Although, the integrated biorefinery systems increase the annual CO_2 and pollutants emissions over 75,000 tons per annum comparing to the conventional Kraft pulp mill, the CO_2 and pollutants reduction are potentially enhanced by the replacement to fossil-based products; as well as, the benefit of electricity supply. Accordingly, the net CO_2 and other pollutants emission for all scenarios of the integrated biorefinery system as well as BLGCC and conventional Kraft process show negative value meaning that the pollutions will be reduced in the global scale. Scenario I, where BLG-based syngas was utilized to produce DME as biofuel, has a smaller potential to reduce net CO_2 comparing to the BLGCC where bioelectricity was generated based on black liquor gasification. However, it could potentially lessen total emissions of the other pollutants by replacing the diesel engine with greener biofuel. Due to the CO_2 capture following by the methanol synthesis, scenario III achieves the highest potential to reduce net CO_2 followed by BLGCC, scenario I, scenario II and the conventional Tomlinson process, respectively. The integrated CCS design (scenario III) can improve the potential of net CO_2 reduction about 20% from BLGCC and 140% from scenario II with 2% enhanced profit comparing to scenario II. The integrated biorefinery without succinic acid (scenario I) provides the net CO_2 reduction 37.5% higher than the system with integrated succinic acid production (scenario II).

On the other hand, the scenarios with the integrated succinic acid process can significantly reduce net SO_x, NO_x and PM10 due to the larger bio-based power generation replacing fossil-based. Unlike the Tomlinson boiler case, all integrated biorefinery systems can reduce net SO_x, NO_x and PM10 emissions, therefore they have potential to lessen the air pollution. Scenario III achieves highest reduction of pollutants followed by scenario II.

Table 25 Environmental impact indicated by net CO_2, SO_x, NO_x and PM10.

Info/Process	Unit	Scenario 1	Scenario 2	Scenario 3	Tomlinson	BLGCC
CO_2 Emission						
Process CO_2 emission	ton/y	158,000	350,000	288,000	47,900	63,200
CO_2 from power import (TH-Grid)	ton/y	0	0	0	33,300	938
Total CO_2 Emission	ton/y	158,000	350,000	288,000	81,200	63,138
CO_2 Reduction						
Grid power replacement (TH-Grid)	ton/y	72,200	151,000	151,000	16,900	52,300
Diesel replacement by DME	ton/y	3,320	3,320	6,470	-	-
Petro-based SA replacement	ton/y	-	33,600	33,600	-	-
Biomass consumption	ton/y	147,000	209,000	209,000	103,000	103,000
Total CO_2 reduction	ton/y	222,520	396,920	400,070	119,900	155,300
Net CO_2 (Emission – Reduction)						
Net CO_2 [a]	ton/y	-64,520	-46,920	-112,070	-38,700	-91,162
Air pollutant Emission						
Total SOx emission	ton/y	35.1	77.2	77.2	149	5.2
Total SOx reduction	ton/y	354	693	736	72.2	224
Net SOx [a]	ton/y	-318.9	-615.8	-658.8	76.8	-218.8
Total NOx emission	ton/y	41	90.3	90.3	50.8	34.4
Total NOx emission	ton/y	143	184	285	8.77	27.2
Net NOx [a]	ton/y	-102	-93.7	-194.7	42.03	7.2
Total PM10 emission	ton/y	3.07	6.76	6.76	45.05	4.51
Total PM10 emission	ton/y	87.9	172	183	17.9	55.4
Net PM10[a]	ton/y	-84.83	-165.24	-176.24	27.15	-50.89

[a] Negative value means the consumption of CO_2 in the process

6.4.4 Comparison of pulp mill receptor

Besides Kraft pulping process, Soda pulping process has also been considered as a receptor of the integrated biorefinery network in the previous work (Mongkhonsiri et al., 2020). The comparisons of the results between scenario I, II and III of the integrated biorefinery-Kraft pulping network and the integrated biorefinery-Soda pulping network with the same feedstock amount are illustrated in Table 26.

The integrated biorefinery-Kraft pulping network requires more supplementary biomass than the integrated biorefinery-Soda pulping network because the bark by-product is 16 ktons per years less than the bagasse pith by-product. However, the larger biomass utilization provides larger bio-electricity supply and environmental benefits. The integrated biorefinery-Kraft pulping network shows higher profit than in the integrated Soda pulping network in all scenarios due to the 4% increased biochemical production. Nonetheless, the process synthesis of the integrated biorefinery-Soda pulping network indicates that it obtains higher profit than the integrated Kraft pulping network because of the pith can be used in the succinic acid production with additional pretreatment step (Mongkhonsiri et al., 2018). That design yields more succinic acid which is a higher-value biochemical. Likewise, the bagasse pith is abundant and contains more cellulose than the wood bark.

Since more biomass is utilized by imported biomass in all scenarios of the integrated biorefinery-Kraft pulping network, the air pollutants emissions reductions are higher than the Soda pulping network. Comparison of the integrated network with gasification-based DME production in scenario I and the scenario IS (similar set-up of the Soda pulping network), the scenario I has 5% lower of the net CO_2 emission and 20% lower of the other pollutants emissions. Similarly, the integrated DME and succinic acid productions network in scenario II lowers the net CO_2 emission up to 40% compare to scenario IIS of the Soda pulping network.

Table 26 Process performance comparison between scenarios of biorefinery system with Kraft pulp mill and with Soda pulp mill

Info/Process	Unit	Integrated Biorefinery in Kraft pulp mill		Integrated Biorefinery in Soda pulp mill	
		Scenario I	Scenario II	Scenario IS	Scenario IIS
Eucalyptus wood /Bagasse	ton/y	100,000	100,000	100,000	100,000
	\$/y	2,900,000	2,900,000	2,300,000	2,300,000
Purchased biomass	ton/y	42,500	102,500	0	59,200
	\$/y	977,500	2,357,500	0	1,360,000
Pulp sale	ton/y	39,510	-	30,700	-
	\$/y	21,493,440	-	9,220,000	-
DME sale	ton/y	5,920	5,920	5,350	5,350
	\$/y	4,025,600	4,025,600	3,640,000	3,640,000
Succinic acid sale	ton/y	-	17,800	-	14,700
	\$/y	-	53,400,000	-	44,400,000
Power sell (+)/buy (-) [a]	MWh	5,800	70,000	-3,240	83,100
	\$/y	580,000	7,000,000	-453,000	11,600,000
Capital & operating cost	\$/y	1,816,000	5,100,000	975,000	4,024,000
Profit	\$/y	20,400,000	54,100,000	9,300,000	52,000,000
Net CO_2 [b]	ton/y	-64,500	-46,900	-61,300	-33,200
Net SOx [b]	ton/y	-319	-615	-185	-561
Net NOx [b]	ton/y	-102	-93.7	-101	-96.9
Net PM10 [b]	ton/y	-84.8	-165	-124	-150

[a] Negative value means power deficit that the purchase of power from other sources is required

[b] Negative value means the consumption of CO_2 in the process

CHAPTER 7

CONCLUSION AND RECOMENDATIONS FOR FUTURE WORKS

7.1 Conclusion

Superstructure optimization has been performed to generate optimal integrated network alternatives considering three scenarios that represent potential future trends for pulp and paper industry transformation. From the results, top value-added biochemicals have been identified, such as succinic acid and lactic acid but not ethanol that could improve the profitability of the pulp mill as well as black liquor gasification with DME production that can supply bioenergy and biofuel. Soda pulping mill is a suitable receptor for the integrated biorefinery. However, Kraft process implemented with succinic acid and lignin extraction is a feasible network even though it has lower profit. Also, the cases with integrated multiple bio-products with/without pulp for paper production illustrate that they provide higher profit than the conventional pulping industry and can respond to the fluctuating market due to its multi-product system. To mitigate risks of low margin pulp mill, it is essential to consider the transformation of integrated biorefinery process in pulp and paper industry as a long-term investment. Superstructure-based process synthesis approach supported by Super-O as a user-friendly software interfaced with the GAMS solver is an effective systematic methodology for the synthesis of integrated biorefinery networks with pulp and paper industry. The case studies solved so far have demonstrated the applicability of the synthesis methodology through Super-O which can manage large and complex problems with a fast problem formulation, robust solution and efficient data management.

The integration of biorefinery framework into the existing pulp mill was examined for the enhancement of sustainability of the integrated process. According to the obtained results, the profitability and the efficiencies in terms of mass and energy utilizations of each biorefinery-integrated process were improved with the acceptably low compromise to the environment. Therefore, the systematic approach decomposed into three stages: synthesis, design, and innovation, was proven capable of providing the sustainable biorefinery system. According to our superstructure optimization results, SA and DME productions integrated into the Soda pulping process appeared the most profitable. Although the integration of SA and DME productions to the pulping process resulted in the required external supply of biomass, the benefit was attained due to the excess electricity for sale and the independency to fossil fuel.

Finally, innovation alternatives created in response to the targets for improvement could reduce the adverse impacts to the environment. The net CO_2 obtained from the innovation alternatives revealed that the solar power could reduce the CO_2 emission by 4% compared to the base case of DME production (Scenario 1) while the obtained profit decreased merely 2%. In case of the integrated SA production process, the methanol synthesis via CO_2 utilization was implemented to synthesize more DME resulting in the lower CO_2 emission; 42% reduction in the CO_2 emission was obtained with the profit decreased only by 0.6%.

Kraft pulp mill can be the receptor of the integrated biorefinery system that provides biomass feedstock; kraft pulp, black liquor and wood bark, feed to both biochemical and thermochemical biorefinery platforms. Rigorous process information was obtained by performing the detailed simulation of the processes. The integrated biorefinery system into the existing kraft pulp mill needs additional biomass import to produce the energy to meet the requirement by the system including kraft pulp mill. Consequently, all scenarios of the integrated biorefinery system can export excess electricity leading to extra profit. Moreover, the additional biomass utilization offers environmental benefits which can be indicated by the reduction of the net CO_2, SO_x NO_x and PM10 emissions. The integrated succinic acid production can significantly improve profitability of the biorefinery network, on the expense of decreasing CO_2 reduction. However, the total emissions of other pollutants, especially SO_x, were reduced due to the higher power generation. Comparing the integrated soda process case, the integrated kraft process achieves 4% higher profit with the integrated succinic acid as a result of more biochemical production. Also, the potential of CO_2 and air pollutants reduction was enhanced by the larger utilized biomass for bioenergy generation. The integrated DME and succinic acid process with CO_2 utilization attains the highest profit as well as the highest pollutants reduction among all studied scenarios by the reason that carbon capture, storage, and utilization leads to more biofuel production. The integrated biorefinery systems into the existing pulp mill were proven to potentially improve the profitability and reduce the environmental impact beyond the conventional mill.

7.2 Recommendations for Future Works

Firstly, the databases of biorefinery technologies should be expanded and gathered. While, there are numerous information in literatures that are disrupted, the systematic data collection leads to the easier and faster solution of process synthesis and design of sustainable biorefinery process for each context. The organized collection in superstructure form provides a useful source of the technologies with more feedstocks, processing pathways and bioproducts as well as future derivatives for next researches. Moreover, the systematic databases allow the effective overview to locate research gaps and development direction. In this study, economic data for superstructure optimization and process evaluation is applied by a single point. However, it would be clearer view of economic performance when sensitivity of economic data is considered by applied fluctuated price of material and energy in different situation.

A systematic framework for the process synthesis and design has potential for development of sustainable biorefinery network for the greener future. The superstructure of biorefinery integrated in pulp mill could be expanded for lignin utilization to produce value-added chemicals after lignin extraction. This lignin utilization has been considered as a promising platform for various remarkable chemicals. Nonetheless, lignin conversion technologies are not massive and not ready for industrial scale. Moreover, other syngas-based bioproducts such as Fischer-Tropsch liquids can be included in consideration and evaluation. Apart from biochemical conversion of cellulose pulp, thermochemical technologies should be applied to convert pulp into other promising biochemicals.

When the system is expanded into larger multiple production of biorefinery supply chain, transportation cost needs to be considered for material transfer between each production sites. Supply chain for multiple bioproduct system can be optimized by superstructure-based process synthesis together with transportation cost based on site location. Correspondingly, market analysis for bioproducts and government policy can be incorporated in decision making supported by superstructure-based approach.

Towards biorefinery process design, heat exchanger network design is also important to make process more effective energy utilization and profitable. Moreover, process intensification should be a future work to debottleneck the process hot-spot for more sustainable of the integrated biorefinery system that may apply a phenomena-based method for synthesis of more sustainable alternatives.

REFERENCES

Abdelaziz, O., Gadalla, M., Ashour, F. 2014. Simulation of biomethanol production from green syngas through sustainable process design. In: The 4th International Conference on Simulation and Modeling Methodologies, Technologies and Applications. Vienna, Austria.

Agency, U.S.E.P., Standards, O.O.A.Q.P. 1995 10.2 Chemical Wood Pulping. In: Compilation of Air Pollutant Emission Factors Volume I: Stationary Point and Area Source, pp.1-18.

Ahmed, A.M.A., Salmiaton, A., Choong, T.S.Y., Wan Azlina, W.A.K.G. 2015. Review of kinetic and equilibrium concepts for biomass tar modeling by using Aspen Plus. Renewable and Sustainable Energy Reviews 52, 1623—1644.

Air Products and Chemicals, Inc. 1993. Synthesis of DME and alternative fuels in the liquid phase from coal-derived synthesis gas, In: report DOE/PC/89865-T8, U.S. Dept. of Energy, Pittsburgh Energy Tech. Center, Pittsburgh, PA. https://www.osti.gov/biblio/10170276-synthesis-dimethyl-ether-alternative-fuels-liquid-phase-from-coal-derived-synthesis-gas-final-technical-report.

Alvarado-Morales, M., Terra, J., Gernaey, K.V., Woodley, J.M., Gani, R., 2009. Biorefining: Computer aided tools for sustainable design and analysis of bioethanol production. Chemical Engineering Research and Design 87(9), 1171-1183.

Anggarani, R., Wibowo, C.S., Rulianto, D. 2014. Application of Dimethyl Ether as LPG Substitution for Household Stove, Energy Procedia 47, 227-234.

Babi, D.K., Holtbruegge, J., Lutze, P., Gorak, A., Woodley, J.M., Gani, R., 2015. Sustainable process synthesis–intensification. Computers & Chemical Engineering 81, 218-244.

Badger, P.C. 2002. Ethanol from cellulose: A general review. In: Janick J., Whipkey, A. (Eds.), Trends in new crops and new uses, ASHS Press, Alexandria, VA, USA.

Bajpai, P. 2011. Integrated Forest Biorefinery. In: Biotechnology for Pulp and Paper Processing, pp. 375-402: Springer US.

Bajpai, P. 2013. Chapter 3 - Emerging biorefinery process options, In Biorefinery in the Pulp and Paper Industry, Academic Press, Boston. 13-17.

Balagurumurthy, B., Singh, R., Ohri, P., Prakash, A., Bhaskar, T. 2015. Thermochemical Biorefinery, 157-174.

Benali, M., Périn-Levasseur, Z., Savulescu, L., Kouisni, L., Jemaa, N., Kudra, T., Paleologou, M. 2014. Implementation of lignin-based biorefinery into a Canadian softwood kraft pulp mill: Optimal resources integration and economic viability assessment. Biomass and Bioenergy 67, 473-482.

Bertran, M.-O., Frauzem, R., Sanchez-Arcilla, A.S., Zhang, L., Woodley, J.M., Gani, R., 2017 A generic methodology for processing route synthesis and design based on superstructure optimization, Computers & Chemical Engineering 106, 892-910.

Blackadder, W.H., Lundberg, H., Rensfelt, E., Waldheim, L., 1994. Heat and power production via gasification in the range 5–50 MWe, In: Bridgwater, A.V. (Ed.), Advances in Biomass Thermochemical Conversion, Balckie Academic & Professional Press, London.

Bozell, J.J., Petersen, G.R. 2010. Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited. Green Chemistry 12(4), 539.

Brodin, M., Vallejos, M., Opedal, M.T., Area, M.C., Chinga-Carrasco, G. 2017. Lignocellulosics as sustainable resources for production of bioplastics – A review, Journal of Cleaner Production 162, 646—664.

Carlsson, P., Wiinikka, H., Marklund, M., Grönberg, C., Pettersson, E., Lidman, M., Gebar, R., 2010. Experimental investigation of an industrial scale black liquor gasifier. 1. The effect of reactor operation parameters on product gas composition, Fuel 89, 4025—4034.

Carvalheiro, F., Duarte, L.C., Gírio, F.M. 2008. Hemicellulose biorefineries: a review on biomass pretreatments. Journal of Scientific and Industrial Research 67(11), 849-864.

Carvalho, A., Matos, H.A., Gani, R. SustainPro—A tool for systematic process analysis, generation and evaluation of sustainable design alternatives. Computers & Chemical Engineering 50 (2013): 8-27.

Chambost, V., Mcnutt, J., Stuart P.R. 2008. Guided tour: Implementing the forest biorefinery (FBR) at existing pulp and paper mills. Pulp & Paper Canada109:7.

Cherubini, F. 2010. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. Energy Conversion and Management 51(7), 1412-1421.

Choi, S., Song, C.W., Shin, J.H., Lee, S.Y. 2015. Biorefineries for the production of top building block chemicals and their derivatives. Metabolic Engineering 28, 223-39.

Consonni, S., Katofsky, R.E., Larson, E.D. 2009. A gasification-based biorefinery for the pulp and paper industry. Chemical Engineering Research and Design 87(9), 1293-1317.

Consonni, S., Larson, E.D. 1996. Biomass gasifier/aeroderivative gas turbine combined cycles: Part B — Performance calculations and economic assessment. Journal of Engineering for Gas Turbines and Power 118 (3), 516—525.

Cukalovic, A., Stevens, C.V. 2008. Feasibility of production methods for succinic acid derivatives: a marriage of renewable resource and chemical technology. Biofuels, Bioproducts and Biorefining 2, 505-529.

d'Anterroches L., Gani, R. 2005. Group contribution based process flowsheet synthesis, design and modelling. Fluid Phase Equilibria 228-229, 141–146.

Datta, R. 1992. Process for the production of SA by anaerobic fermentation. United States patent 5143833A.

Doherty, B., Rainey, T. 2006. Bagasse Fractionation by the Soda Process. In: Hogarth, D (Ed.) Proceedings of the Australian Society of Sugar Cane Technologists, 2-5 May 2006, Australia, Queensland, Mackay.

Donnelly, M., Millard, C., Stols, L. 1998. Mutant E.coli strain with increased succinic acid production. U.S. patent 5,770,435.

Douglas, J.M. 1985 A hierarchical decision procedure for process synthesis. AIChE Journal, 31(3):353–362.

Dries, L., Klomp, J., van Ophem, J., Zhu, X. 2016. Social science perspectives on the bio-economy. NJAS - Wageningen Journal of Life Sciences 77, 1-4.

Duran, M.A., Grossmann, I.E. 1986. A mixed-integer nonlinear programming algorithm for process systems synthesis. AIChE Journal., 32(4), 592–606.

EIA (Online), 2020. https://www.eia.gov/naturalgas/.

Eriksson, H., Harvey, S. 2004. Black liquor gasification-consequences for both industry and society. Energy. 29, 581-612.

Farhad, S., Saffar‐Avval, M., Younessi‐Sinaki, M. 2008. Efficient design of feedwater heaters network in steam power plants using pinch technology and exergy analysis. International Journal of Energy Research 32(1), 1-11.

Frauzem, R. 2017. Sustainable process design with process intensification – Development and implementation of a framework for sustainable carbon dioxide capture and utilization processes. Doctoral Dissertation. Technical University of Denmark (DTU), Kgs. Lyngby, Denmark.

Frauzem, R., Kongpanna, P., Roh, K., Lee, J.H., Pavarajarn, V., Assabumrungrat, S., Gani, R., 2015. Chapter 7 - Sustainable process design: Sustainable process networks for carbon dioxide conversion. Computer Aided Chemical Engineer 36, 175-195.

Gassner, M., Maréchal, F. 2009. Methodology for the optimal thermo-economic, multi-objective design of thermochemical fuel production from biomass. Computers & Chemical Engineering33, 769–781.

Gatti, M., Marechal, F., Martelli, E., Consonni, S. 2013. Thermodynamic analysis, energy integration and flowsheet improvement of a methanol absorption acid gas removal process. Chemical Engineering Transactions 35, 1974━9791.

Gea, G., Sanchez, J.L., Murillo, M.B., Arauzo, J. 2004. Kinetics of CO2 gasification of alkaline black liquor from wheat straw. Influence of CO and CO2 concentrations on the gasification rate. Industrial & Engineering Chemistry 43, 3233-3241.

Ghayur, A., Verheyen, T.V., Meuleman, E. 2019. Techno-economic analysis of a SA biorefinery coproducing acetic acid and DME. Journal of Cleaner Production 230, 1165━1175.

Glassner, D.A., Elankovan, P., Beacom, D.R., Berglund, K.A. 1995. Purification process for succinic acid produced by fermentation. Applied Biochemistry and Biotechnology. 73, 51-52.

Gogate, M.R., Vijayaraghavan, P. 1992. A single━stage, liquid-phase DME synthesis process from syngas: thermodynamic analysis of the LPDME process system. Fuel Science and Technology International 10, 281━311.

Graaf, G.H., Beenackers, A.A.C.M., 1996. Comparison of two━phase and three━phase methanol synthesis processes, Chemical Engineering and Processing 35 (6), 413━427. Green Car Congress (Online), 2008. Retrieve from: https://www.greencarcongress.com/2008/09/biodme-projects.html.

Grossmann, I.E. 1990. Mixed-integer nonlinear programming techniques for the synthesis of engineering systems. Research in Engineering Design 1(3-4), 205–228.

Grossmann, I.E. 2002. Review of nonlinear mixed-integer and disjunctive programming techniques. Optimization and Engineering, 3(3), 227–252.

Guettler, M.V., Jain, M.K., Soni, B.K. 1998. Process for making succinic acid, microorganisms for use in the process and methods of obtaining the microorganisms. U.S. patent 5,723,322.

Guettler, M.V., Rumler, D., Jain, M.K. 1999. Actinobacillus succinogenes sp. nov., a novel succinic-acid-producing strain from the bovine rumen. International Journal of Systematic and Evolutionary Microbiology 49, 207-216.

Hämäläinen, S., Näyhä, A., Pesonen, H.-L. 2011. Forest biorefineries. A business opportunity for the Finnish forest cluster. Journal Cleaner Production 19, 1884─1891.

Hannula, I., Kurkela, E. 2012. A parametric modelling study for pressurised steam/O_2-blown fluidised-bed gasification of wood with catalytic reforming. Biomass & Bioenergy 38, 58─67.

Harmsen, P.F.H., Hackmann, M.M., Bos, H.L. 2014. Green building blocks for bio-based plastics. Biofuels, Bioproducts & Biorefining 8, 306-324.

Hedstrom, J. 2014. Simulation and assessment of carbon capture processes applied to a pulp mill. MSc Thesis, Innovative and Sustainable Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden.

Hilpmann, G., Becher, N., Pahner, F.-A., Kusema, B., Mäki-Arvela, P., Lange, R., Murzin D.Y., Salmi, T. 2016. Acid hydrolysis of xylan, Catalysis Today 259 (Part 2), 376-380.

Hostrup, M., Gani, R., Kravanja, Z., Sorsak, A., Grossmann, I. 2001. Integration of thermodynamic insights and MINLP optimization for the synthesis, design and analysis of process flowsheets. Computers & Chemical Engineering 25(1), 73–83.

IRENA, 2012. Renewable energy technologies: Cost analysis of solar photovoltaics. IRENA working Paper, Vol. 1: Power Sector Issue 4/5. The International Renewable Energy Agency. Available at: https://www.irena.org/publications/2012/Jun/Renewable-Energy-Cost-Analysis---Solar-Photovoltaics (20.08.19).

IRENA, 2018. Renewable power generation costs in 2017. The International Renewable Energy Agency. Available at: https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2018/Jan/IRENA_2017_Power_Costs_2018.pdf (20.08.19).

Jafri, Y., Furusjö, E., Kirtania, K., Gebart, R., 2016. Performance of a pilot-scale entrained flow black liquor gasifier. Energy Fuels 30, 3175–3185.

Jaksland, C.A., Gani, R. 1996. An integreated approach to process/product design and synthesis based on properties-process relationship. Computers & Chemical Engineering 20(96), S151–S156

Jaksland, C.A., Gani, R., Lien K.M. 1995. Separation process design and synthesis based on thermodynamic insights. Chemical Engineering Science 50(3), 511–530.

Janssen, M. 2012. Market potential of biorefinery products. in Sandén, B. and Pettersson, K. (Eds.),Systems Perspectives on Biorefineries, pp. 30-41: Chalmers University of Technology.

Janssen, M. 2013. Market potential of biorefinery products. 30-41. DOI:10.13140/2.1.1157.6007.

Kajaste, R. 2014. Chemicals from biomass — managing greenhouse gas emissions in biorefinery production chains — a review. Journal of Cleaner Production 75, 1—10.

Kalakul, S., Malakul, P., Siemanond, K., Gani, R. 2014. Integration of life cycle assessment software with tools for economic and sustainability analyses and process simulation for sustainable process design. Journal of Cleaner Production 71, 98–109.

Kanchanalai, P., Temani, G., Kawajiri, Y., Realff, M.J. 2016. Reaction kinetics of concentrated—acid hydrolysis for cellulose and hemicellulose and effect of crystallinity. BioResources 11 (1), 1672—1689.

Kaushal, P. and Tyagi R. 2017. Advanced simulation of biomass gasification in a fluidized bed reactor using ASPEN PLUS. Renewable Energy 101, 629—636.

Khoo, H., Eufrasio-Espinosa, R.M., Koh, L.S.C., Sharratt, P.N., Isoni, V. 2019. Sustainability assessment of biorefinery production chains: A combined LCA-supply chain approach. Journal of Cleaner Production 235, 1116–1137.

Kocis G.R., Grossmann, I.E. 1987. Relaxation strategy for the structural optimization of process flow sheets. Industrial & Engineering Chemistry 26(9),1869–1880.

Kocis G.R., Grossmann, I.E. 1989 A modelling and decomposition strategy for the minlp optimization of process flowsheets. Computers & Chemical Engineering 13(7), 797–819.

Kongpanna, P., Babi, D.K., Pavarajarn, V., Assabumrungrat, S., Gani, R. 2016. Systematic methods and tools for design of sustainable chemical processes for CO2 utilization. Computers & Chemical Engineering 87, 125-144.

Kong-Win Chang, J., Duret, X., Berberi, V., Zahedi-Niaki, H., Lavoie, J.M. 2018. Two-step thermochemical cellulose hydrolysis with partial neutralization for glucose production. Frontiers in Chemistry 6:117.

Kouhia, M., Holmberg, H., Ahtila, P. 2015. Microalgae-utilizing biorefinery concept for pulp and paper industry: Converting secondary streams into value-added products. Algal Research 10, 41-47.

Kurzrock, T., Weuster-Botz, D. 2010. Recovery of succinic acid from fermentation broth. Biotechnology Letters 32, 331-339.

Larson, E., Consonni, S., Katofsky, R. 2003. A cost-benefit assessment of biomass gasification power generation in the pulp and paper industry. Final report. Princeton University and Politecnico di Milano.

Larson, E., Consonni, S., Katofsky, R. 2006a. A cost-benefit assessment of gasification-based biorefining in the kraft pulp and paper industry, Volume 1 Main Report. Princeton University and Politecnico di Milano.

Larson, E.D., Consonni, S., Katofsky, R., Campbell, M., Iisa K., Frederick, W.J. 2006b. A cost-benefit assessment of gasification-based biorefining in the Kraft pulp and paper industry. Princeton University and Politecnico di Milano, Volume 3: Fuel Chain and National Cost-Benefit Analysis.

Larson, E.D., Consonni, S., Napoletano, S., Katofsky, R.E., Iisa, K., Frederick, J. 2006c. A cost-benefit assessment of gasification-based biorefining in the Kraft pulp and paper industry. Princeton University and Politecnico di Milano, Volume 2 Detailed Biorefinery Design and Performance Simulation.

Larson, E.D., Tingjin, R., 2003. Synthetic fuel production by indirect coal liquefaction. Energy for Sustainable Development, Vol. VII, NO.4.

Lee, H. 2015. Development of lactic and SA biorefinery configurations for integration into a thermomechanical pulp mill. MSc Thesis. University of Montreal, Montreal, Canada. Retrieved at: https://publications.polymtl.ca/1750 (12.01.19).

Lee, L.C., Lee, S.Y., Hong, S.H., Chang, H.N., Park, S.C. 2003. Biological conversion of wood hydrolysate to succinic acid by Anaerobiospirillum succiniciproducens. Biotechnology Letters 25, 111-114.

Lee, P.C., Lee, S.Y., Hong, S.H., Chang, H.N. 2002. Isolation and characterization of a new succinic acid-producing bacterium, Mannheimia succiniciproducens MBEL55E, from bovine rumen. Applied Microbiology and Biotechnology 58, 663-668.

Lee, S., Gogate, M.R., Kulik, C.J. 1992. A novel single-step dimethyl Ether (DME) synthesis in a three-phase slurry reactor from co-rich syngas. Chemical Engineering Science 47, 3769─3776.

Lee, S., Grossmann, I.E. 2003. Global optimization of nonlinear generalized disjunctive programming with bilinear equality constraints: applications to process networks. Computers & Chemical Engineering 27(11), 1557–1575.

Li, H., McDonald, A.G. 2014. Fractionation and characterization of industrial lignins. Industrial Crops and Products 62, 67-76.

Li, Q., Wang, D., Wu, Y., Li, W., Zhang, Y., Xing, J., Su, Z., 2010. One step recovery of succinic acid from fermentation broths by crystallization. Separation and Purification Technology 72, 294-300.

Lindblom, M., Landälv, I., 2007. Chemrec's atmospheric & pressurized BLG (Black Liquor Gasification) technology – Status and future plans, In: Proceeding International Chemical Recovery Conference, Quebec City, QC, Canada.

Lourençon, T.V., Hansel, F.A., da Silva, T.A., Ramos, L.P., de Muniz, G.I.B., and Magalhães, W.L.E. 2015. Hardwood and softwood kraft lignins fractionation by simple sequential acid precipitation. Separation and Purification Technology 154, 82-88.

Luque, R., Lin, C.S.K, Du, C., Macquarrie, D.J., Koutinas, A., Wang, R., Webb, C., Clark, J.H. 2009. Chemical transformations of succinic acid recovered from fermentation broths by a novel direct vacuum distillation-crystallisation method. Green Chemistry 11, 193–200.

Lutze, P., Babi, D.K., Woodley, J.M., and Gani, R. Phenomena Based Methodology for Process Synthesis Incorporating Process Intensification. Industrial & Engineering Chemistry Research 52(22) (2013): 7127-7144.

Mansoornejad, B., Chambost, V., and Stuart, P. 2010. Integrating product portfolio design and supply chain design for the forest biorefinery. Computers & Chemical Engineering 34(9), 1497-1506.

Mansoornejad, B., Pistikopoulos, E.N., and Stuart, P.R. 2013. Scenario-based strategic supply chain design and analysis for the forest biorefinery using an operational supply chain model. International Journal of Production Economics 144(2), 618-634.

Manzardo, A., Ren, J., Piantella, A., Mazzi, A., Fedele, A., Scipioni, A., 2014. Integration of water footprint accounting and costs for optimal chemical pulp supply mix in paper industry. Journal of Cleaner Production 72, 167–173.

Marinova, M., Mateos-Espejel, E., Jemaa, N., Paris, J. 2009. Addressing the increased energy demand of a Kraft mill biorefinery: The hemicellulose extraction case. Chemical Engineering Research and Design 87(9), 1269-1275.

Martín, M., Grossmann, I.E. 2016. Enhanced production of methanol from switchgrass: CO2 to methanol. In: Kravanja Z. and Bogataj, M. (Eds.), 26th European Symposium on Computer Aided Process Engineering, volume 38, pp. 43–48, Portorož, Slovenia, Elsevier BV.

Maryam, M., Mariya, M., Michel, P., Jean, P. 2013. The forest biorefinery and its implementation in the pulp and paper industry. Energy overview. Applied Thermal Engineering 50(2), 1427-1436.

MEA Thailand (Online), 2020. https://www.mea.or.th/profile/109/114.

Menon, V., Rao, M. 2012. Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. Progress in Energy and Combustion Science 38(4), 522-550.

Mészáros I., Fonyó, Z. 1986. A new bounding strategy for synthesizing distillation schemes with energy integration. Computers & Chemical Engineering 10(6), 545–550.

Mizsey P., Fonyo, Z. 1990. Toward a more realistic overall process synthesis-the combined approach. Computers & Chemical Engineering 14(11), 1213–1236.

Mongkhonsiri, G., Charoensuppanimit, P., Anantpinijwatna, A., Gani, R., Assabumrungrat, S. 2020. Process development of sustainable biorefinery system integrated into the existing pulping process. Journal of Cleaner Production 255, 120─278

Mongkhonsiri, G., Gani, R., Malakul, P., Assabumrungrat, S. 2018. Integration of the biorefinery concept for the development of sustainable processes for pulp and paper industry. Computers & Chemical Engineering 119, 70–84.

Morales, M., Ataman, M., Badr, S., Linster, S., Kourlimpinis, I., Papadokonstantakis, S., Hatzimanikatis, V., Hungerbühler, K. 2016. Sustainability assessment of SA production technologies from biomass using metabolic engineering. Energy & Environmental Science 9, 2794─2805.

Morschbacker, A. 2009. Bio-ethanol based ethylene. Polymer Reviews 49, 79-84.

Mtunzi, B., Mampwheli, N., Meyer, E., Mungwena, W. 2012. Bagasse-based co-generation at Hippo Valley Estates sugar factory in Zimbabwe. Journal of Energy in Southern Africa 23, 15-22.

Naqvi, M., Yan, J., Dahlquist, E. 2010. Black liquor gasification integrated in pulp and paper mills: A critical review. Bioresource Technology 101, 8001-8015.

Neiva, D., Fernandes, L., Araújo, S., LourenÇo¸ A., Gominho, J., Simões, R., Pereira, H. 2015. Chemical composition and kraft pulping potential of 12 eucalypt species. Industrial Crops and Products 66, 89—95.

New York and Geneva. 2008. Biofuel production technologies: status, prospects and implications for trade and development, United Nations Conference on Trade and Development. United Nations. Retrieved from https://digitallibrary.un.org/record/1315430/files/%5ETD_%5EUNCTAD_DITC_TED_2007_10-EN.pdf.

Ng, K.L., Chadwick, D., Toseland, B.A. 1999. Kinetics and modeling of DME synthesis from synthesis gas. Chemical Engineering Science 54 (15—16), 3587—3592.

Nilsson, B. 1993. Reactor for gasification of cellulose-waste liquors especially black liquor. Chemrec AB. US patent: US5407455A.

Okino, S., Inui, M., Yukawa, H. 2005. Production of organic acids by Corynebacterium glutamicum under oxygen deprivation. Applied Microbiology and Biotechnology 8, 475-480.

Patrick, K. 2003. Gasification edges closer to commercial reality with three new N.A. Mill startups. In: PaperAge, pp. 30-33.

Per, T. 2010. The LignoBoost Process. Cellulose Chemistry and Technology 44(1-3), 53-58.

Pinazo, J.M., Domine, M.E., Parvulescu, V., Petru, F. 2015. Sustainability metrics for succinic acid production: A comparison between biomass-based and petrochemical routes. Catalysis Today 239, 17-24.

Prosim, 2015. Syngas Deacidification with Rectisol Process. Avaiable at: http://www.prosim.net/bibliotheque/File/Exemples-Applications-PSP/En/PSPS_E14_EN-Rectisol-Process.pdf.

Quaglia, A., Gargalo, C.L., Chairakwongsa, S., Sin, G., Gani, R., 2015. Systematic network synthesis and design: Problem formulation, superstructure generation, data management and solution. Computers & Chemical Engineering 72, 68-86.

Quaglia, A., Pennati, A., Bogataj, M., Kravanja, Z., Sin, G., Gani R. 2014.Industrial process water treatment and reuse: A framework for synthesis and design. Industrial & Engineering Chemistry Research 53(13), 5160–5171

Quaglia, A., Sarup, B., Sin, G., Gani, R. 2012. Integrated business and engineering framework for synthesis and design of enterprise-wide processing networks. Computers & Chemical Engineering 38, 213–223.

Quaglia, A., Sarup, B., Sin, G., Gani, R. 2013. A systematic framework for enterprise-wide optimization: Synthesis and design of processing networks under uncertainty. Computers & Chemical Engineering 59, 47-62.

Rafione, T., Marinova, M., Montastruc, L., Paris, J. 2014. The Green Integrated Forest Biorefinery: An innovative concept for the pulp and paper mills. Applied Thermal Engineering 73(1), 74-81.

Ragauskas, A.J., Beckham, G.T., Biddy, M.J., Chandra, R., Chen, F., Davis, M.J., Davison, B.H., Dixon, R.A., Gilna, P., M .Keller, M., Langan, P., Naskar, A.K., Saddler, J.N., Tschaplinski, T.J., Tuskan, G., Wyman, C.E. 2014. Lignin valorization: improving lignin processing in the biorefinery. Science. 344(6185),1246843.

Ragauskas, A.J., Nagy, M., Kim, D.H., Eckert, C.A., Hallett, J.P., and Liotta, C.L. 2006. From wood to fuels: Integrating biofuels and pulp production. Industrial Biotechnology 2(1), 55-65.

Raimo, A. 2015. Pulp Mills and Wood-Based Biorefineries. Retieved from: https://en.wikipedia.org/wiki/Kraft_process.

Raman, R.I., Grossmann, I.E. 1994. Modelling and computational techniques for logic based integer programming. Computers & Chemical Engineering 18(7), 563–578.

Ranke, G., Weiss, H., 1982. Separation of gaseous components from a gaseous mixture by physical scrubbing. United States patent 4324567.

Research and Markets, 2016. The ethylene technology report 2016 - Research and markets. Retrieved from: www.researchandmarkets.com.

Rizwan, M., Lee, J.H., Gani, R. 2013. Superstructure optimization of biodiesel production from microalgal biomass. Computers & Chemical Engineering 46, 111-116.

Rizwan, M., Lee, J.H., Gani, R. 2015. Optimal design of microalgae-based biorefinery: economics, opportunities and challenges. Applied Energy 150, 69–79.

Santos, P.S.B.d., Erdocia, X., Gatto, D.A., Labidi, J. 2014. Characterisation of kraft lignin separated by gradient acid precipitation. Industrial Crops and Products 55, 149-154.

Saturnino, D.M. 2012. Modeling of Kraft mill chemical balance. Doctoral Dissertation, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Ontario, Canada.

Schlesinger, R., Götzinger, G., Sixta, H., Friedl, A., Harasek, M. 2006. Evaluation of alkali resistant nanofiltration membranes for the separation of hemicellulose from concentrated alkaline process liquors. Desalination 192, 303-314.

Siirola, J.J. 1996. European Symposium on Computer Aided Process Engineering-6Strategic process synthesis: Advances in the hierarchical approach. Computers & Chemical Engineering 20, S1637-S1643.

Simell, P., Kurkela, E., Stfthlberg, P., Hepola, J. 1996. Catalytic hot gas cleaning of gasification gas. Catalysis Today 27 (1─2), 55─62.

Spath, P.L., Dayton, D.C. 2003. Preliminary screening technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas, National Renewable Energy Laboratory, NREL/TP-510-34929.

Springfield, R., Hester, R.D. 1999. Continuous ion-exclusion chromatography system for acid/sugar separation. Separation Science and Technology 34 (6─7), 1217─1241.

Toledano, A., García, A., Mondragon, I., Labidi, J. 2010. Lignin separation and fractionation by ultrafiltration. Separation and Purification Technology 71, 38-43.

Tomani, P., 2010. The lignoboost process. Cellulose Chemistry and Technology 44, 53-58.

Tomani, P., Axegard, P., Berglin, N., Lovell, A., Nordgren, D. 2011. Integration of lignin removal into a kraft pulp mill and use of lignin as a biofuel. Cellulose Chemistry and Technology. 45, 533-540.

Tomani, P., Ohman, F., Theliander, H., Axegard, P. 2012. Separaing lignin from black liquor by precipitation, suspension and separation. U.S. Patent 8,172,981 B2.

Towers, M., Browne, T., Kerekes, R., Paris, J., Tran, H. 2007. Biorefinery opportunities for the Canadian pulp and paper industry. Pulp & Paper Canada, Business Information Group. T109-112.

Turkay, M., Grossmann, I.E. 1998. Structural flowsheet optimization with complex investment cost functions. Computers & Chemical Engineering 22(4-5), 673–686.

Ulrika, W., Paul, S. 2006. Identifying the Canadian Forest Biorefinery. Pulp & Paper Canada, Business Information Group. T128-133.

Volvo brochure, 2012. Available at: https://www.aboutdme.org/aboutdme/files/ccLibraryFiles/Filename/000000002392/BioDME_Volvo_brochure.pdf.

Wallberg, O., Jönsson, A.S., Wimmerstedt, R. 2003. Ultrafiltration of kraft black liquor with a ceramic membrane. Desalination. 156, 145-153.

Walton, S.L., Hutto D., Genco J.M., van Walsum G.P., van Heiningen A.R.P. 2010. Pre-extraction of hemicelluloses from hardwood chips using an alkaline wood pulping solution followed by kraft pulping of the extracted wood chips. Industrial & Engineering Chemistry Research 49, 12638-12645.

Wang, G., Chen, H. 2013. Fractionation of alkali-extracted lignin from steam exploded stalk by gradient acid precipitation. Separation and Purification Technology 105, 98-105.

Weastra, S.R.O. 2012. WP 8.1 Determination of market potential for selected platform chemicals. Itaconic acid, Succinic acid, 2,5-furandicarboxylic acid. Retrieved from http:// www.bioconsept.eu/wp-content/uploads/BioConSepT_Market-potential-for-selected-platform-chemicals_report1.pdf.

Weizhen, Z. 2015. Precipitation of Kraft Lignin: Yield and Equilibrium. Doctoral Dissertation, Department of Chemistry and Chemical Engineering Chalmers University of Technology, Sweden.

Werpy, T., Petersen, G. 2004. Top Value Added Chemicals from Biomass: Volume I -- Results of Screening for Potential Candidates from Sugars and Synthesis Gas. in Other Information: PBD: 1 Aug 2004. Medium: ED.

Whitty, K., Nilsson, A. 2001. Experience from a high temperature, pressurized black liquor gasification pilot plant. In: Proceedings of the Tappi Chemical International Recovery Conference, Tappi Press, Atlanta, pp. 655-662.

Wijaya, Y.P., Dhewangga, R.D., Putra, Widyaya, V.T., Ha, J.-M., Dong J.S., Kim, C.S. 2014. Comparative study on two-step concentrated acid hydrolysis for the extraction of sugars from lignocellulosic biomass. Bioresource Technology 164, 221–231.

Wooley, R., Ruth, M., Sheehan, J., Ibsen, K., Majdeski, H., Galvez, A.1999. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis current and futuristic scenarios. Technical Report, TP-580-26157. National Renewable Energy Laboratory (NREL).

Xiang, Y., Cai, L., Guan, Y., Liu, W., He, T., Li, J. 2019. Study on the biomass-based integrated gasification combined cycle with negative CO_2 emissions under different temperatures and pressures. Energy 179, 571—580.

Yanagisawa, M., Shibata, I., Isogai, A. 2005. SEC-MALLS analysis of softwood kraft pulp using LiCl/1,3-dimethyl-2-imidazolidinone as an eluent. Cellulose 12(2), 151-158.

Yuan, Z., Chen, B., Gani, R. 2013. Applications of process synthesis: Moving from conventional chemical processes towards biorefinery processes. Computers & Chemical Engineering 49, 217-229.

Zafar. S., 2019 The concept of biorefinery. Retrieved from: https://www.bioenergyconsult.com/tag/biorefinery-platforms/

Zhu, W. 2015. Precipitation of Kraft Lignin Yield and Equilibrium. Doctoral thesis, Chalmers University of Technology, Sweden.

Zondervan, E., Nawaz, M., de Haan, A.B.A.B., Woodley, J.M., Gani, R. 2011. Optimal design of a multi-product biorefinery system. Computers & Chemical Engineering 35, 1752–1766.

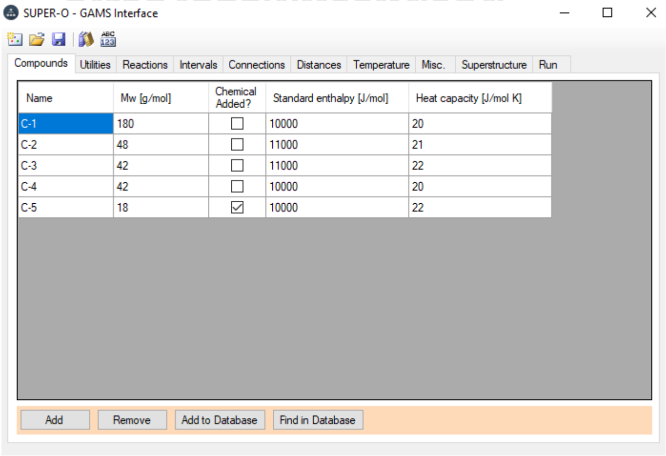
APPENDICES

Appendix A: Super-O feature

As Section 3.1.2 mention, Super-O is applied for systematically data collection to implementation of certain steps in Stage I. Super-O include 10 tabs to insert the technical and economic data:

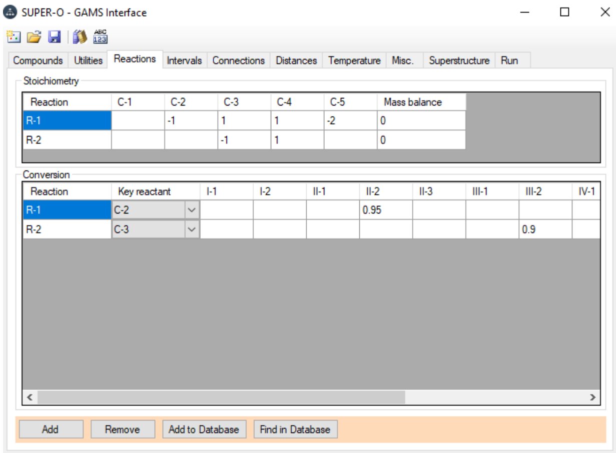
1) “Compounds” is to define all components involved in superstructure
2) “Utility” is to define all utilities considered in superstructure
3) “Reactions” is to collect reaction information occurred in each interval, involving stoichiometry of reaction and conversion of key component.
4) “Intervals” shows a list of all interval in each step. Here, equation for capital cost estimation from feed inlet of the interval can be given. Also, Waste removal (SW), product separation (split), chemical and utility added for each interval can be insert by the proper faction based on mathematical model of interval (See in Appendix B).
5) “Connections” is to define all connections between interval as the possible processing pathway. Intervals which is connected is inserted “1” in Connection table. Regarding to Primary outlet table, primary connection and secondary connection are identified. Primary connection that means primary product from the previous interval (Column) is sent to next interval (Row) is shown with “1” in green highlight. Secondary connection that means secondary product from the previous interval (Column) is sent to next interval (Row) is shown without “1” in green highlight. Primary and secondary product was defined by separation (split) fraction in “Intervals” tab.

6) “Distances” is to insert data for transportation between interval when each interval is not in the same site. It is employed to calculate transportation cost but was not considered in this work.
7) “Temperature” is to calculate utility use and heat exchanger network for utility and heat exchanger cost. It was also not considered in this work.
8) “Misc” is miscellanea data input window include feed flow rate, raw material cost, product price, chemical and utility cost that is insert by value per unit, also production life.
9) “Superstructure” overviews all intervals and steps with their connections in the superstructure.
10) “Run” is to GAMS integration. This window shows address of input file to call, GAMS file containing model for optimization and output file that appear when the optimization is done, and console window. the optimization results are shown in the “console" textbox, and the user could open the result excel file (output file) for detail results.



Name	Mw [g/mol]	Chemical Added?	Standard enthalpy [J/mol]	Heat capacity [J/mol K]
C-1	180	☐	10000	20
C-2	48	☐	11000	21
C-3	42	☐	11000	22
C-4	42	☐	10000	20
C-5	18	☑	10000	22

Figure A.1 Compounds data



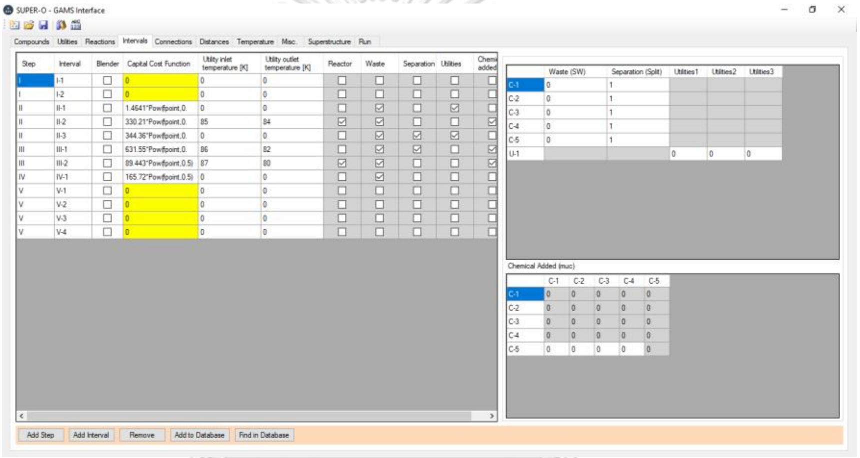
Stoichiometry

Reaction	C-1	C-2	C-3	C-4	C-5	Mass balance
R-1		-1	1	1	-2	0
R-2			-1	1		0

Conversion

Reaction	Key reactant	I-1	I-2	II-1	II-2	II-3	III-1	III-2	IV-1
R-1	C-2				0.95				
R-2	C-3							0.9	

Figure A.2 Reactions data



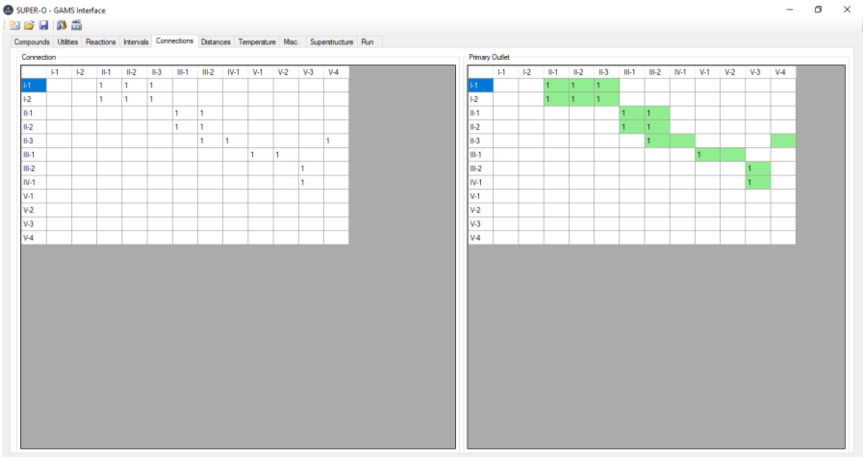
Step	Interval	Blender	Capital Cost Function	Utility inlet temperature [K]	Utility outlet temperature [K]	Reactor	Waste	Separation	Utilities	Chemi added
I	I-1	☐	0	0	0	☐	☐	☐	☐	☐
I	I-2	☐	0	0	0	☐	☐	☐	☐	☐
II	II-1	☐	1.4641*Pow(fpoint,0.	0	0	☐	☑	☐	☑	☐
II	II-2	☐	330.21*Pow(fpoint,0.	85	84	☑	☑	☐	☐	☑
II	II-3	☐	344.36*Pow(fpoint,0.	0	0	☐	☑	☑	☑	☐
III	III-1	☐	631.55*Pow(fpoint,0.	86	82	☐	☑	☑	☐	☑
III	III-2	☐	89.443*Pow(fpoint,0.5)	87	80	☑	☑	☐	☐	☑
IV	IV-1	☐	165.72*Pow(fpoint,0.5)	0	0	☐	☑	☐	☐	☐
V	V-1	☐	0	0	0	☐	☐	☐	☐	☐
V	V-2	☐	0	0	0	☐	☐	☐	☐	☐
V	V-3	☐	0	0	0	☐	☐	☐	☐	☐
V	V-4	☐	0	0	0	☐	☐	☐	☐	☐

	Waste (SW)	Separation (Split)	Utilities1	Utilities2	Utilities3
C-1	0	1			
C-2	0	1			
C-3	0	1			
C-4	0	1			
C-5	0	1			
U-1			0	0	0

Chemical Added (muc)

	C-1	C-2	C-3	C-4	C-5
C-1	0	0	0	0	0
C-2	0	0	0	0	0
C-3	0	0	0	0	0
C-4	0	0	0	0	0
C-5	0	0	0	0	0

Figure A.3 intervals data



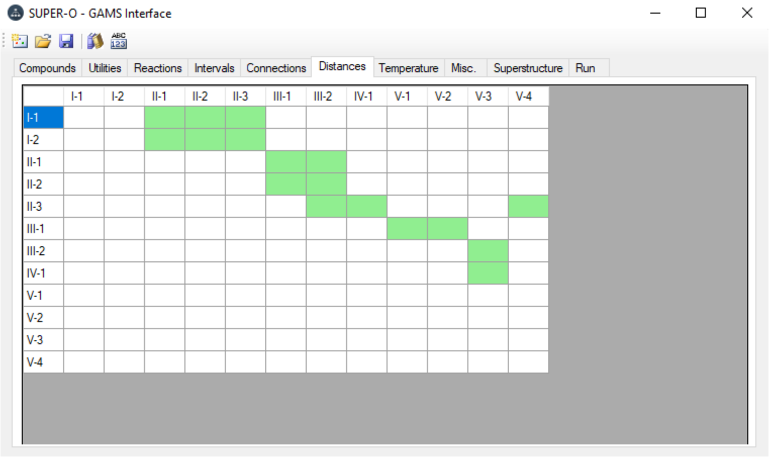
Connection

	I-1	I-2	II-1	II-2	II-3	III-1	III-2	IV-1	V-1	V-2	V-3	V-4
I-1			1	1	1							
I-2			1	1	1							
II-1						1	1					
II-2						1	1					
II-3							1	1				1
III-1									1	1		
III-2											1	
IV-1											1	
V-1												
V-2												
V-3												
V-4												

Primary Outlet

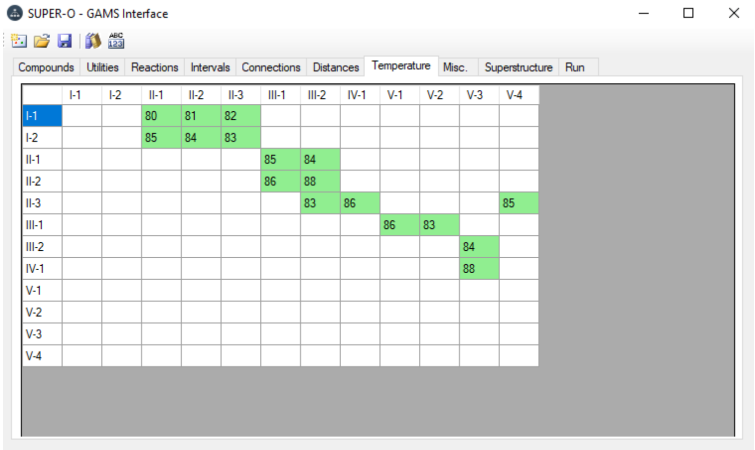
	I-1	I-2	II-1	II-2	II-3	III-1	III-2	IV-1	V-1	V-2	V-3	V-4
I-1			1	1	1							
I-2			1	1	1							
II-1						1	1					
II-2						1	1					
II-3							1					
III-1									1			
III-2											1	
IV-1											1	
V-1												
V-2												
V-3												
V-4												

Figure A.4 Connections data



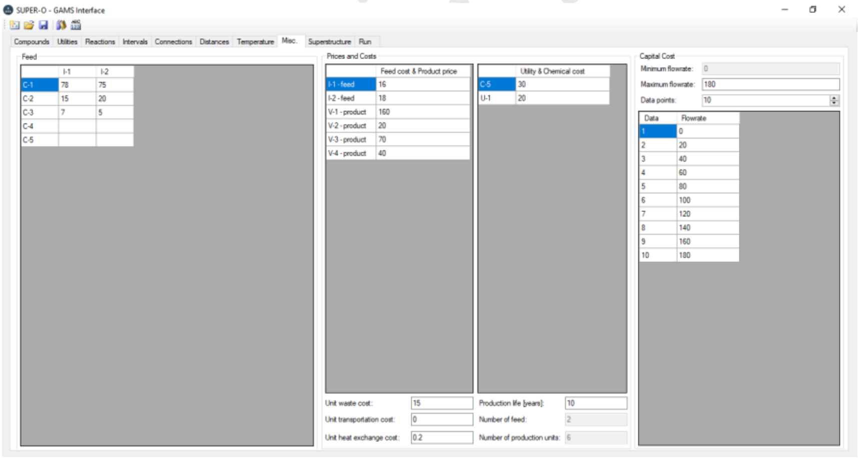
	I-1	I-2	II-1	II-2	II-3	III-1	III-2	IV-1	V-1	V-2	V-3	V-4
I-1			🟩	🟩	🟩							
I-2			🟩	🟩	🟩							
II-1						🟩	🟩					
II-2						🟩	🟩					
II-3							🟩	🟩				🟩
III-1									🟩	🟩		
III-2											🟩	
IV-1											🟩	
V-1												
V-2												
V-3												
V-4												

Figure A.5 Distances data



	I-1	I-2	II-1	II-2	II-3	III-1	III-2	IV-1	V-1	V-2	V-3	V-4
I-1			80	81	82							
I-2			85	84	83							
II-1						85	84					
II-2						86	88					
II-3							83	86				85
III-1									86	83		
III-2											84	
IV-1											88	
V-1												
V-2												
V-3												
V-4												

Figure A.6 Temperature data



Feed

	I-1	I-2
C-1	78	75
C-2	15	20
C-3	7	5
C-4		
C-5		

Prices and Costs

	Feed cost & Product price
I-1 - feed	16
I-2 - feed	18
V-1 - product	160
V-2 - product	20
V-3 - product	70
V-4 - product	40

	Utility & Chemical cost
C-5	30
U-1	20

Unit waste cost: 15
Unit transportation cost: 0
Unit heat exchange cost: 0.2
Production life [years]: 10
Number of feed: 2
Number of production units: 6

Capital Cost

Minimum flowrate: 0
Maximum flowrate: 180
Data points: 10

Data	Flowrate
1	0
2	20
3	40
4	60
5	80
6	100
7	120
8	140
9	160
10	180

Figure A.7 Miscellanea data

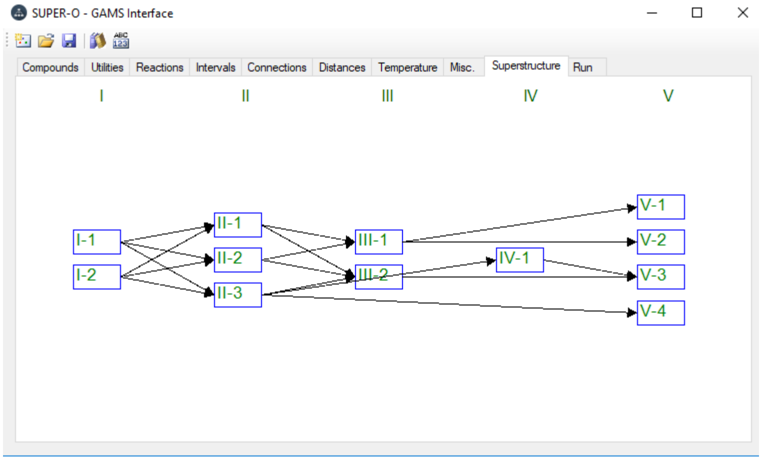
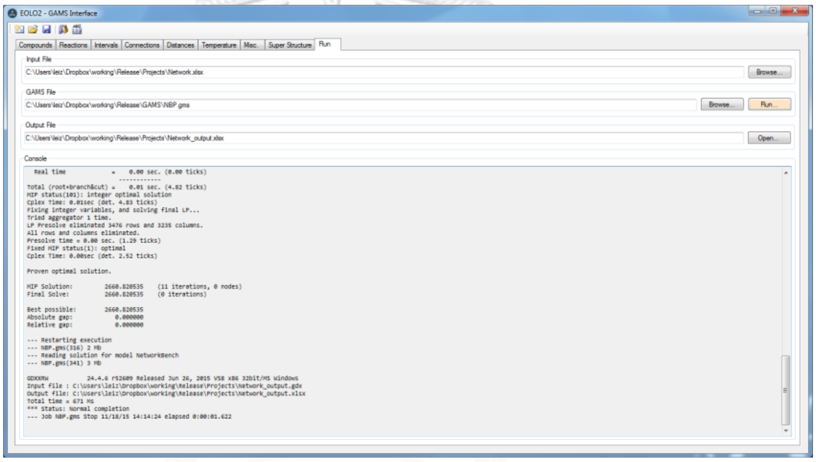


Figure A.8 Superstructure visualization



Input File
C:\Users\leiz\Dropbox\working\Release\Projects\Network.xlsx

GAMS File
C:\Users\leiz\Dropbox\working\Release\GAMS\NBP.gms

Output File
C:\Users\leiz\Dropbox\working\Release\Projects\Network_output.xlsx

Console

```
  Real time             =    0.00 sec. (0.00 ticks)
                          ------------
Total (root+branch&cut) =    0.01 sec. (4.82 ticks)
MIP status(101): integer optimal solution
Cplex Time: 0.01sec (det. 4.83 ticks)
Fixing integer variables, and solving final LP...
Tried aggregator 1 time.
LP Presolve eliminated 3476 rows and 3235 columns.
All rows and columns eliminated.
Presolve time = 0.00 sec. (1.29 ticks)
Fixed MIP status(1): optimal
Cplex Time: 0.00sec (det. 2.52 ticks)

Proven optimal solution.

MIP Solution:         2660.820535    (11 iterations, 0 nodes)
Final Solve:          2660.820535    (0 iterations)

Best possible:        2660.820535
Absolute gap:            0.000000
Relative gap:            0.000000

--- Restarting execution
--- NBP.gms(316) 2 Mb
--- Reading solution for model NetworkBench
--- NBP.gms(341) 3 Mb

GDXXRW           24.4.6 r52609 Released Jun 26, 2015 VS8 x86 32bit/MS Windows
Input file : C:\Users\leiz\Dropbox\working\Release\Projects\Network_output.gdx
Output file: C:\Users\leiz\Dropbox\working\Release\Projects\Network_output.xlsx
Total time = 671 Ms
*** Status: Normal completion
--- Job NBP.gms Stop 11/18/15 14:14:24 elapsed 0:00:01.622
```

Figure A.9 GAMS integration

Appendix B: Mathematical model of superstructure representation

The mathematical programming problem, process constraints, logical constraints and the variable bounds are formulated as a mixed integer (non)linear programming problem or MI(N)LP model. This is described by the set of equations (2)-(22) (Quaglia et al., 2015).

The superstructure representation also includes a list of decision variables that determine the connections between intervals from one processing step to another.

Mathematical model of superstructure optimization

Objective function

$$Max\ Z = \sum_{i}\sum_{k} P_k^P f_{i,k}^W - \sum_{i}\sum_{kk} P_{kk}^{RW} f_{i,kk}^W - \sum_{kk}\sum_{i} P_i^C g_{i,kk}^M - \sum_{kk}\sum_{j} P_j^U g_{i,kk}^U - \frac{\sum_{kk} invl_{kk}}{\tau} \tag{1}$$

Process interval equation

Chemical added

$$g_{i,kk}^M = \sum_{ii} \mu_{i,ii,kk} f_{i,k}^{IN} \tag{2}$$

Reaction

$$f_{i,kk}^R = f_{i,kk}^M + \sum_{rr,react} f_{react,kk}^M\, \theta_{react,kk,rr} \cdot \frac{\gamma_{i,kk,rr}}{\gamma_{i,kk,rr}} \cdot \frac{MW_i}{MW_{react}} \tag{3}$$

Waste separation

$$f_{i,kk}^W = f_{i,kk}^R (1 - \delta_{i,kk}) \tag{4}$$

$$g_{j,kk}^W = f_{i,kk}^R - f_{i,kk}^W \tag{5}$$

Utility consumption

$$g_{j,kk}^U = g_{j,kk}^{U,1} + g_{j,kk}^{U,2} + g_{j,kk}^{U,3} \tag{6}$$

$$g_{j,kk}^{U,1} = \beta_{j,kk}^1 \sum_{ii} f_{ii,kk}^{IN} \tag{7}$$

$$g_{j,kk}^{U,2} = \beta_{j,kk}^2 \sum_{ii} f_{ii,kk}^{M} \tag{8}$$

$$g_{j,kk}^{U,3} = \beta_{j,kk}^3 \sum_{ii} f_{ii,kk}^{W} \tag{9}$$

Product separation

$$f_{i,kk}^{OUT,P} = f_{i,kk}^W \sigma_{i,kk} \tag{10}$$

$$f_{i,kk}^{OUT,S} = f_{i,kk}^W - f_{i,kk}^{OUT,P} \tag{11}$$

Capital cost

$$invl_{kk} = f(f_{i,kk}^W) \tag{12}$$

Superstructure flow model

$$f_{i,k,kk}^2 \le f_{i,k}^{OUT,S} (S_{k,kk} - SP_{i,kk}) \tag{13}$$

$$f_{i,k}^{OUT,P} = \sum_{kk} f_{i,k,kk}^1 \tag{14}$$

$$f_{i,k}^{OUT,S} = \sum_{kk} f_{i,k,kk}^2 \tag{15}$$

$$f_{i,kk}^1 \le f_{i,kk}^{OUT,P} SP_{k,kk} \tag{16}$$

$$f_{i,k,kk} = f^1_{i,k,kk} + f^2_{i,k,kk} \tag{17}$$

$$f^{IN}_{i,kk} = \sum_k f_{i,k,kk} \tag{18}$$

Superstructure logical constraint

$$\sum_{kk} y_{kk}\ \upsilon_{kk,step} \leq 1 \tag{19}$$

$$f^{W}_{i,kk} \leq y_{kk} M \tag{20}$$

$$g^{M}_{i,kk} \leq y_{kk} M \tag{21}$$

$$\sum_{i} f^{IN}_{i,kk} \leq y_{kk} M \tag{22}$$

Nomenclature

Continuous variables

Z	Objective function
f	Component flow rate
g	Added/Removed component
invl	Capital cost of processing interval

Binary variables

y	Selection of processing intervals

Parameters

P	Fixed cost
MW	Molecular weight
S	Superstructure connection (binary)
SP	Superstructure primary connection (binary)
M	Large number for Big-M
β	Specific consumption of utility with reference to stream flowrate in utility point
δ	Fraction waste separation
γ	Stoichiometric coefficient
μ	Ratio of chemical consumption based on reference component
υ	Allocation of intervals to a processing step
σ	Fraction separation of primary product
θ	Conversion
τ	Project lifetime

Subscripts

i	Component
ii	Reference component
j	Utility
k	Processing interval (Origin)
kk	Processing interval (Destination)
rr	Reaction
react	Key reactant, a subset of i
step	Processing step

Superscripts

P	Product
RW	Raw material
C	Chemical Added
U	Utility
IN	Inlet in a processing interval
M	Outlet of mixing task
R	Outlet of reaction task
W	Outlet of waste separation task
OUT,P	Primary outlet of product separation task
OUT,S	Second outlet of product separation task

Appendix C: Input data for the superstructure generation

The data for superstructure generation was collected by input file via Super-O feature. The input data mainly reactions for model formulation are provided in tables.

Table C.1 List of intervals

	$U^{k;st}$	Step								
		1	2	3	4	5	6	7	8	9
Interval	Eucalyptus-RW	1								
	Bagasse-RW	1								
	Debarking-PPREI		1							
	Depithing-PPREI		1							
	Kraft proces-PP			1						
	Soda process-PP			1						
	KraftBLEvap-BLE				1					
	SodaBLEvap-BLE				1					
	Lime-PT					1				
	Dilute acid-PT					1				
	Steam explosion-PT					1				
	Ammonia fiber explosion-PT					1				
	Ammonia recycle percolation-PT					1				
	Bark Combustion-PT					1				
	Pith combustion-PT					1				
	NREL-HYD						1			
	Concentrated acid-HYD						1			
	Dilute acid-HYD						1			
	NREL-PHYD							1		
	Concentrated acid-PHYD							1		
	Dilute acid-PHYD							1		
	Kraft Bark							1		
	Soda Bark							1		
	Filtration								1	
	Lactic acid Fermentation-FERM									1

	Ethanol fermentation-FERM									1
	Succinic acid fermentationDC-FERM									1
	Succinic acid fermentationED-FERM									1
Interval	$\mathbf{U}^{k;st}$	10	11	12	13	14	15	16	17	18
	LA Filtration-SolSepI	1								
	EtOH Filtration-SolSepI	1								
	SA FiltrationDC-SolSepI	1								
	SA FiltrationED-SolSepI	1								
	LA Precipitation-SEPI		1							
	BeerDistillation-SEPI		1							
	SA Electrodialysis-SEPI		1							
	Gypsum Separation-SolSepII			1						
	LA Evaporation-SEPII				1					
	SA EvaporationDC-SEPII				1					
	SA EvaporationED-SEPII				1					
	MeOH Esterification-PURI					1				
	Rect/Zeolite-PURI					1				
	Rect/Silica-PURI					1				
	SolExt/Glycerol-PURI					1				
	SolExt/Ethylene glycol-PURI					1				
	IL/EMIM-BF4-PURI					1				
	IL/BMIM-Cl-PURI					1				
	SA CrystallizationDC-PURI					1				
	SA CrystallizationED-PURI					1				
	SA DryingDC-PURII						1			
	SA DryingED-PURII						1			
	Tomlinson Boiler-BLU							1		
	BLGCC-BLU							1		
	BLGDMEa-BLU							1		
	BLGDMEb-BLU							1		
	BLGDMEc-BLU							1		
	LigninExtraction-BLU							1		
	Lactic acid-BCP								1	

	$U^{k;st}$	10	11	12	13	14	15	16	17	18
Interval	Ethanol-BCP								1	
	Succinic acidDC-BCP								1	
	Succinic acidED-BCP								1	
	KraftPulp-PPROD								1	
	SodaPulp-PPROD								1	
	ElectricityTSB-BLUP									1
	ElectricityBLGCC-BLUP									1
	DMEaBLG-BLUP									1
	DMEbBLG-BLUP									1
	DMEcBLG-BLUP									1
	LigninLE-BLUP									1
	BlackliquorLE-BLUP									1
	Bark-Energy									1
	Pith-Energy									1

List of process steps

1 Raw material
2 Pulping pretreatment
3 Pulping process
4 Black liquor evaporation
5 Pretreatment
6 Hydrolysis
7 Pulp Hydrolysis
8 Sugar Division
9 Fermentation
10 Solid Separation I
11 Separation I
12 Solid Separation II
13 Separation II
14 Purification I
15 Purification II
16 Energy Production
17 Bioproduct
18 Biofuel & Energy

Table C.2.1 Reaction stoichiometry

$\boldsymbol{\gamma}^{i;kk;rr}$	BLGCC	BLGDMEa	BLGDMEb	BLGDMEc
Lignin	-1	-1	-1	-1
Electricity to Grid	1			
DMEa		1		
DMEb			1	
DMEc				1

Table C.2.2 Reaction stoichiometry

$\boldsymbol{\gamma}^{i;kk;rr}$	PT-DA-1	PT-DA-2	PT-DA-3	PT-DA-4
Glucan				
Xylan	-1			
Galactan			-1	
Arabinan		-1		
Mannan				-1
Water	-0.97376	-0.98343	-0.98343	-0.98343
Xylose	0.991254			
Galactose			0.994475	
Mannose				0.994475
Arabionose		0.994475		
Sol-Lignin				

Furfural	0.008746	0.005525		
HMF			0.005525	0.005525

Table C.2.3 Reaction stoichiometry

$\gamma^{i;kk;rr}$	PT-DA-5	PT-DA-6	PT-DA-7	PT-DA-8
Glucan		-1	-1	
Lignin				-1
Water		-0.5	-1	
Sulfuric acid	-1			
Glucose			1	
Sol-Lignin				1
Cellobiose		0.5		
Calciumsulfatedihydrate	1			
Calcium hydroxide	-1			

Table C.2.4 Reaction stoichiometry

$\gamma^{i;kk;rr}$	PT-STEX-1	PT-STEX-2	PT-STEX-3	PT-STEX-4
Glucan	-1			
Xylan		-1		
Galactan				
Arabinan			-1	

Mannan				
Lignin				-1
Water	-0.63854	0.551502	0.540976	
Glucose	0.879514			
Xylose		0.482833		
Arabionose			0.486362	
Sol-Lignin				1
Furfural		0.517167	0.513629	
HMF	0.120486			

Table C.2.5 Reaction stoichiometry

$\gamma^{i;kk;rr}$	PT-STEX-1	PT-STEX-2	PT-STEX-3	PT-STEX-4
Glucan	-1			
Xylan		-1		
Galactan				
Arabinan			-1	
Mannan				
Lignin				-1
Water	-0.63854	0.551502	0.540976	
Glucose	0.879514			
Xylose		0.482833		

Arabionose			0.486362	
Sol-Lignin				1
Furfural		0.517167	0.513629	
HMF	0.120486			

Table C.2.6 Reaction stoichiometry

$\gamma^{i;kk;rr}$	PT-ARP-1	PT-ARP-2	PT-ARP-3
Glucan	-1		
Xylan		-1	
Lignin			-1
Water	-1	-1	
Glucose	1		
Xylose		1	
Sol-Lignin			1

Table C.2.7 Reaction stoichiometry

$\gamma^{i;kk;rr}$	PT-AFEX-1	PT-AFEX-2	PT-AFEX-3	PT-AFEX-4	PT-AFEX-5
Xylan	-1				
Galactan			-1		
Arabinan		-1			
Mannan				-1	

Lignin					-1
Water	-1	-1	-1	-1	
Xylose	1				
Galactose			1		
Mannose				1	
Arabionose		1			
Sol-Lignin					1

Table C.2.8 Reaction stoichiometry

$\gamma^{i;kk;rr}$	HYD-CONCA-1	HYD-CONCA-2	HYD-CONCA-3	HYD-CONCA-4	HYD-CONCA-5
Glucan	-1				
Xylan		-1			
Galactan				-1	
Arabinan					-1
Mannan			-1		
Water	0.999684	-0.98195	-0.99957	-0.93409	-0.75229
Glucose	0.999895				
Xylose		0.993982			
Galactose				0.97803	
Mannose			0.999857		

Arabionose					0.917431
Furfural		0.006018			0.082569
HMF	0.000105		0.000143	0.02197	

Table C.2.9 Reaction stoichiometry

γ $^{i;kk;rr}$	HYD-DILA-1	HYD-DILA-2	HYD-DILA-3	HYD-DILA-4	HYD-DILA-5
Glucan	-1				
Xylan			-1		
Galactan		-1			
Arabinan				-1	
Mannan					-1
Water	0.155738	-0.87101	-0.99815	-0.92108	-0.99768
Glucose	0.614754				
Xylose			0.999382		
Galactose		0.957002			
Mannose					0.999227
Arabionose				0.973695	
Furfural			0.000618	0.026305	
HMF	0.385246	0.042998			0.000773

Table C.2.10 Reaction stoichiometry

$\gamma^{i;kk;rr}$	HYD-NREL-1
Glucan	-1
Water	-1
Glucose	1

Table C.2.11 Reaction stoichiometry

$\gamma^{i;kk;rr}$	FERM-LA-1	FERM-LA-2
Glucose	-1	
Xylose		-1
Lactic acid	2	1.666667

Table C.2.12 Reaction stoichiometry

$\gamma^{i;kk;rr}$	FERM-EtOH-1	FERM-EtOH-2	FERM-EtOH-3	FERM-EtOH-4	FERM-EtOH-5
Acetic acid			3		
Water		-2			
Oxygen	0.000695	1			0.001321
Carbondioxide	1.997196				1.661381
Sulfuric acid					
Glucose	-1	-1	-1	-1	
Xylose					-1

Lactic acid				2	
Ethanol	1.998632				1.664024
Succinic acid	0.00139				0.002643
Glycerol		2			

Table C.2.13 Reaction stoichiometry

$\gamma^{i;kk;rr}$	FERM-EtOH-6	FERM-EtOH-7	FERM-EtOH-8	FERM-EtOH-9
Acetic acid				2.5
Water	-1.66667	-1		
Oxygen	0.833333	0.5		
Xylose	-1	-1	-1	-1
Lactic acid			1.666667	
Glycerol	1.666667			
Xylitol		1		

Table C.2.14 Reaction stoichiometry

$\gamma^{i;kk;rr}$	FERM-SA-1	FERM-SA-2	FERM-SA-3	FERM-SA-4	CONV-LA-1
Acetic acid			1	3	
Water	0.857143	0.714286			
Carbondioxide	-0.85714	-0.71429	-1		

Sulfuric acid					-1
Glucose	-1		-1	-1	
Xylose		-1			
Calciumsulfatedihydrate					1
Calcium hydroxide					-1
Succinic acid	1.714286	1.428571	1		
Formic acid			1		

Table C.3.1 Reaction conversion of key component

$\theta^{react;rr;kk}$	Key Reactant	Dilute acid-PT	Lime-PT	Steam explosion-PT
PT-DA-1	Xylan	0.8575		
PT-DA-2	Arabinan	0.905		
PT-DA-3	Galactan	0.905		
PT-DA-4	Mannan	0.905		
PT-DA-5	Calcium hydroxide	1		
PT-DA-6	Glucan	0.007		
PT-DA-7	Glucan	0.065		
PT-DA-8	Lignin	0.05		
PT-STEX-1	Glucan			0.25696
PT-STEX-2	Xylan			0.07456
PT-STEX-3	Arabinan			0.08224

PT-STEX-4	Lignin			0.582
PT-LIME-1	Glucan		0.022	
PT-LIME-2	Xylan		0.32	
PT-LIME-3	Arabinan		0.61	
PT-LIME-4	Lignin		0.67	

Table C.3.2 Reaction conversion of key component

$\theta_{react;rr;kk}$	Key Reactant	Ammonia fiber explosion-PT	Ammonia recycle percolation-PT	Concentrated acid-HYD
PT-ARP-1	Glucan		0.08	
PT-ARP-2	Xylan		0.57	
PT-ARP-3	Lignin		0.84	
PT-AFEX-1	Xylan	0.5		
PT-AFEX-2	Arabinan	0.5		
PT-AFEX-3	Galactan	0.5		
PT-AFEX-4	Mannan	0.5		
PT-AFEX-5	Lignin	0.33		
HYD-CONCA-1	Glucan			0.9501
HYD-CONCA-2	Xylan			0.893376
HYD-CONCA-3	Mannan			0.98014
HYD-CONCA-4	Galactan			0.7055

HYD-CONCA-5	Arabinan			0.763

Table C.3.3 Reaction conversion of key component

$\theta^{react;rr;kk}$	Key Reactant	Dilute acid-PT	Lime-PT	Steam explosion-PT
PT-DA-1	Xylan	0.8575		
PT-DA-2	Arabinan	0.905		
PT-DA-3	Galactan	0.905		
PT-DA-4	Mannan	0.905		
PT-DA-5	Calcium hydroxide	1		
PT-DA-6	Glucan	0.007		
PT-DA-7	Glucan	0.065		
PT-DA-8	Lignin	0.05		
PT-STEX-1	Glucan			0.25696
PT-STEX-2	Xylan			0.07456
PT-STEX-3	Arabinan			0.08224
PT-STEX-4	Lignin			0.582
PT-LIME-1	Glucan		0.022	
PT-LIME-2	Xylan		0.32	
PT-LIME-3	Arabinan		0.61	
PT-LIME-4	Lignin		0.67	

Table C.3.4 Reaction conversion of key component

$\theta^{react;rr;kk}$	Key Reactant	Dilute acid-HYD	NREL-HYD	LA Precipitation-SEPI
HYD-DILA-1	Glucan	0.0976		
HYD-DILA-2	Galactan	0.7419		
HYD-DILA-3	Xylan	0.9706		
HYD-DILA-4	Arabinan	0.64702		
HYD-DILA-5	Mannan	0.97075		
HYD-NREL-1	Glucan		0.812	
CONV-LA-1	Calcium hydroxide			1

Table C.3.5 Reaction conversion of key component

$\theta^{react;rr;kk}$	Key Reactant	Ethanol fermentation-FERM	Lactic acid Fermentation-FERM	Succinic acid fermentation-FERM
FERM-LA-1	Glucose		0.85	
FERM-LA-2	Xylose		0.8	
FERM-EtOH-1	Glucose	0.92064		
FERM-EtOH-2	Glucose	0.02		
FERM-EtOH-3	Glucose	0.022		
FERM-EtOH-4	Glucose	0.013		
FERM-EtOH-5	Xylose	0.85135		

FERM-EtOH-6	Xylose	0.002			
FERM-EtOH-7	Xylose	0.006			
FERM-EtOH-8	Xylose	0.014			
FERM-EtOH-9	Xylose	0.024			
FERM-SA-1	Glucose				0.75
FERM-SA-2	Xylose				0.43
FERM-SA-3	Glucose				0.05
FERM-SA-4	Glucose				0.2
CONV-LA-1					

Table C.4 Raw material feed

$\o^{i;kk}$	Eucalyptus-RW	Bagasse-RW
Glucan	37739.84	33460
Xylan	9768.56	14560
Galactan	546	609
Arabinan	1087	1589
Mannan	1424	651
Lignin	23222.4	14980
Ash	610	2723
Acetic acid	2002.2	1428
Extractive	0	0
Water	23600	30000

Table C.5 Estimation equation for capital cost

Lime-PT	459.59*(fpoint^0.62)
Dilute acid-PT	105.92*(fpoint^0.62)
Steam explosion-PT	7.4296*(fpoint^0.62)
Ammonia fiber explosion-PT	100.28*(fpoint^0.62)
Ammonia recycle percolation-PT	44.224* (fpoint^0.62)
Bark Combustion-PT	0
Pith combustion-PT	0
NREL-HYD	1167.8*(fpoint^0.62)
Concentrated acid-HYD	194.58*(fpoint^0.62)
Dilute acid-HYD	100.68*(fpoint^0.62)

NREL-PHYD	1167.8*(fpoint^0.62)
Concentrated acid-PHYD	194.58*(fpoint^0.62)
Dilute acid-PHYD	100.68*(fpoint^0.62)
Filtration-SD	85.67053*(fpoint^0.6)
Lactic acid Fermentation-FERM	725.4544*(fpoint^0.6)
Ethanol fermentation-FERM	5*1209.2*(fpoint^0.62)
Succinic acid fermentationDC-FERM	725.4544*(fpoint^0.6)
Succinic acid fermentationED-FERM	725.4544*(fpoint^0.6)
LA Filtration-SolSepI	85.67053*(fpoint^0.6)
EtOH Filtration-SolSepI	85.67053*(fpoint^0.6)
SA FiltrationDC-SolSepI	85.67053*(fpoint^0.6)
SA FiltrationED-SolSepI	85.67053*(fpoint^0.6)
LA Precipitation-SEPI	725.4544*(fpoint^0.6)
BeerDistillation-SEPI	5*899.4638*Pow(fpoint^0.68)
SA Electrodialysis-SEPI	13,200+(7.205234*(fpoint^0.6))
Gypsum Separation-SolSepII	85.67053*(fpoint^0.6)
LA Evaporation-SEPII	899.4638*(fpoint^0.68)
SA EvaporationDC-SEPII	899.4638*(fpoint^0.68)
SA EvaporationED-SEPII	899.4638*(fpoint^0.68)
MeOH Esterification-PURI	(405.7829*2*(fpoint^0.6))+(749.574*2*(fpoint^0.7))+(899.4638*(fpoint^0.68))
Rect/Zeolite-PURI	75.716*(fpoint^0.99)
Rect/Silica-PURI	10.395*(fpoint^0.96)
SolExt/Glycerol-PURI	2*(fpoint^0.62)
SolExt/Ethylene glycol-PURI	2*(fpoint^0.62)
IL/EMIM-BF4-PURI	3.9*(fpoint^0.62)
IL/BMIM-Cl-PURI	3.9*(fpoint^0.62)
SA CrystallizationDC-PURI	441.103*(fpoint^0.6)
SA CrystallizationED-PURI	441.103*(fpoint^0.6)

SA DryingDC-PURII	63*(fpoint^0.6)
SA DryingED-PURII	63*(fpoint^0.6)
Tomlinson Boiler-BLU	0
BLGCC-BLU	460.05*(fpoint^1)
BLGDMEa-BLU	531.356*(fpoint^1)
BLGDMEb-BLU	876.959*(fpoint^1)
BLGDMEc-BLU	683.028*(fpoint^1)
LigninExtraction-BLU	19.0556*(fpoint^1)

Abbreviation

RW	Raw material step
PPRE	Pulping pretreatment step
PP	Pulping process
PT	Pretreatment step for biochemical production
HYD	Hydrolysis step
PHYD	Pulp hydrolysis step
SD	Sugar division step
FERM	Fermentation step
DC	Succinic acid with direct crystallization
EC	Succinic acid with electrodialysis and crystallization
SolSep	Solid separation step
SEP	Separation step
PUR	Purification step

BLU	Black liquor utilization
BCP	Biochemical production
PPROD	Pulping product
BLUP	Product from black liquor utilization
BLGCC	Black liquor gasification combined cycle
BLGDME	Black liquor gasification for DME production
TSB	Tomlinson boiler
CONCA	Concentrated acid
DA or DILA	Dilute acid
STEX	Stream explosion
AFEX	Ammonia fiber explosion
ARP	Ammonia recycle percolation
SA	Succinic acid
LA	Lactic acid
EtOH	Ethanol
fpoint	Feed flow rate of interval

Appendix D: Stream table from process simulation of integrated biorefinery in Soda pulping process

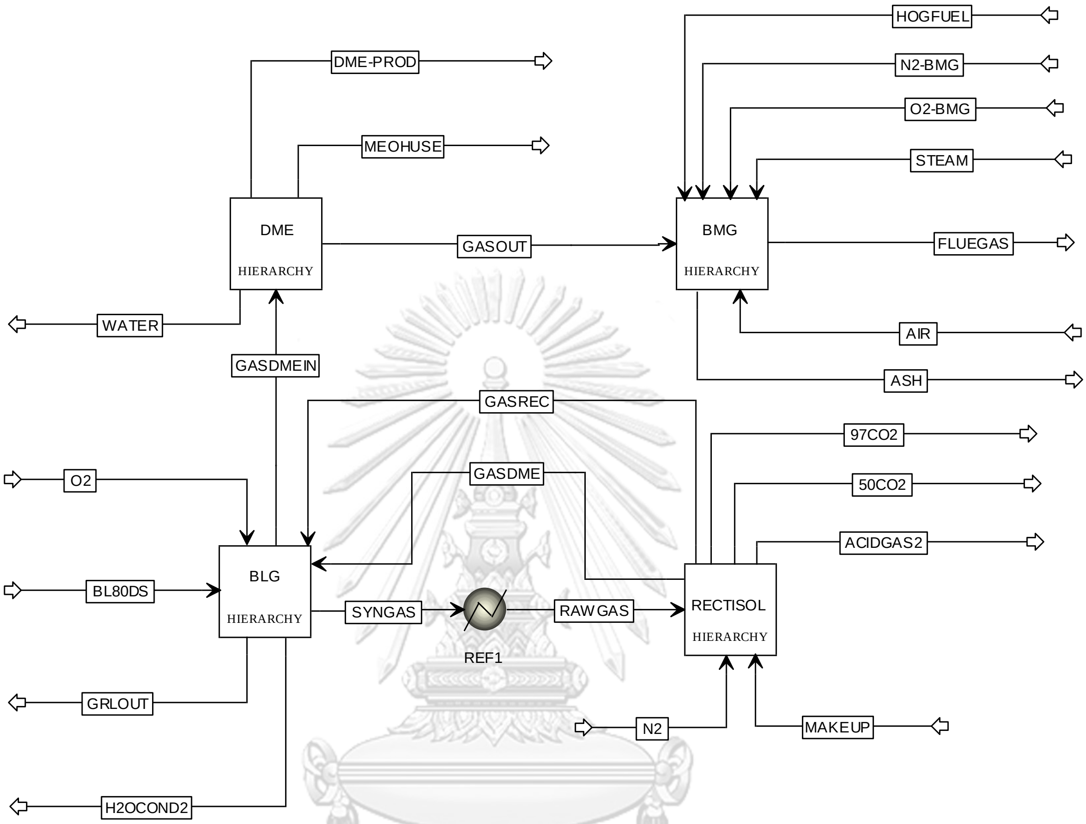


Figure D.1 Gasification-based biorefinery flow diagram

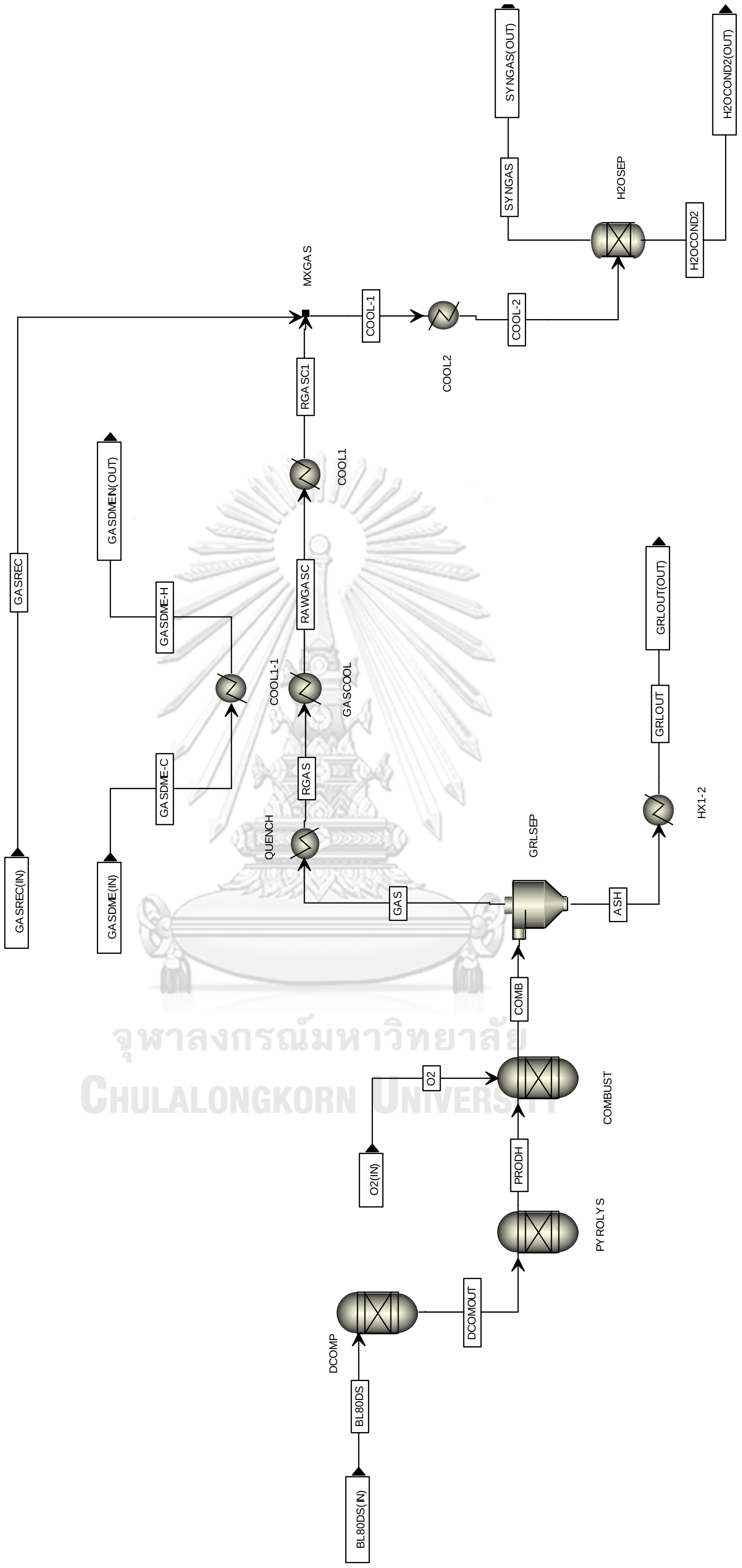


Figure D.2 Black liquor gasification flow diagram

Table D.1 Stream table for black liquor gasification section

	Units	BL80DS	DCOMOUT	GAS	GASDME-C	GASDME-H	O2	RGASC1	SYNGAS
Substream: ALL									
Mass Flow	KG/HR	2535	2535	2613	1379	1379	720	2613	2181
Temperature	C	115	1000	1000	17	100	145	104	35
Pressure	BAR	35.0	33.2	35.0	35.0	32.9	32.9		
Substream: MIXED									
Mass Flow	KG/HR	0	1160	2613	1379	1379	720	2613	2181
Vapor Fraction			1.0000	1.0000	1.0000	1.0000	1.0000	0.8270	1.0000
Liquid Fraction			0.0000	0.0000	0.0000	0.0000	0.0000	0.1730	0.0000
Component Mass Fraction		0	1	1	1	1	1	1	1
C			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O			0.4368	0.1890	0.0000	0.0000	0.0000	0.1890	0.0000
N2			0.0175	0.0110	0.0208	0.0208	0.0117	0.0110	0.0133
H2			0.0793	0.0340	0.0644	0.0644	0.0000	0.0340	0.0411
O2			0.4585	0.0000	0.0000	0.0000	0.9430	0.0000	0.0000
S			0.0079	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CL2			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO2			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO			0.0000	0.4658	0.8794	0.8794	0.0000	0.4658	0.5668
CO2			0.0000	0.2776	0.0009	0.0009	0.0000	0.2776	0.3508
SO			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR			0.0000	0.0125	0.0233	0.0233	0.0452	0.0125	0.0153
H2S			0.0000	0.0036	0.0000	0.0000	0.0000	0.0036	0.0043
COS			0.0000	0.0003	0.0000	0.0000	0.0000	0.0003	0.0003
NH3			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4			0.0000	0.0063	0.0112	0.0112	0.0000	0.0063	0.0078
METHANOL			0.0000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0000
Substream: CIPSD									
Mass Flow	KG/HR	0	732	0	0	0	0	0	0
Component Mass Fraction		0	1	0	0	0	0	0	0
C			1.0000						
Substream: NCPSD									
Mass Flow	KG/HR	2535	642	0	0	0	0	0	0
Component Mass Fraction		1	1	0	0	0	0	0	0
BL		1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ASH		0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HOGFUEL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

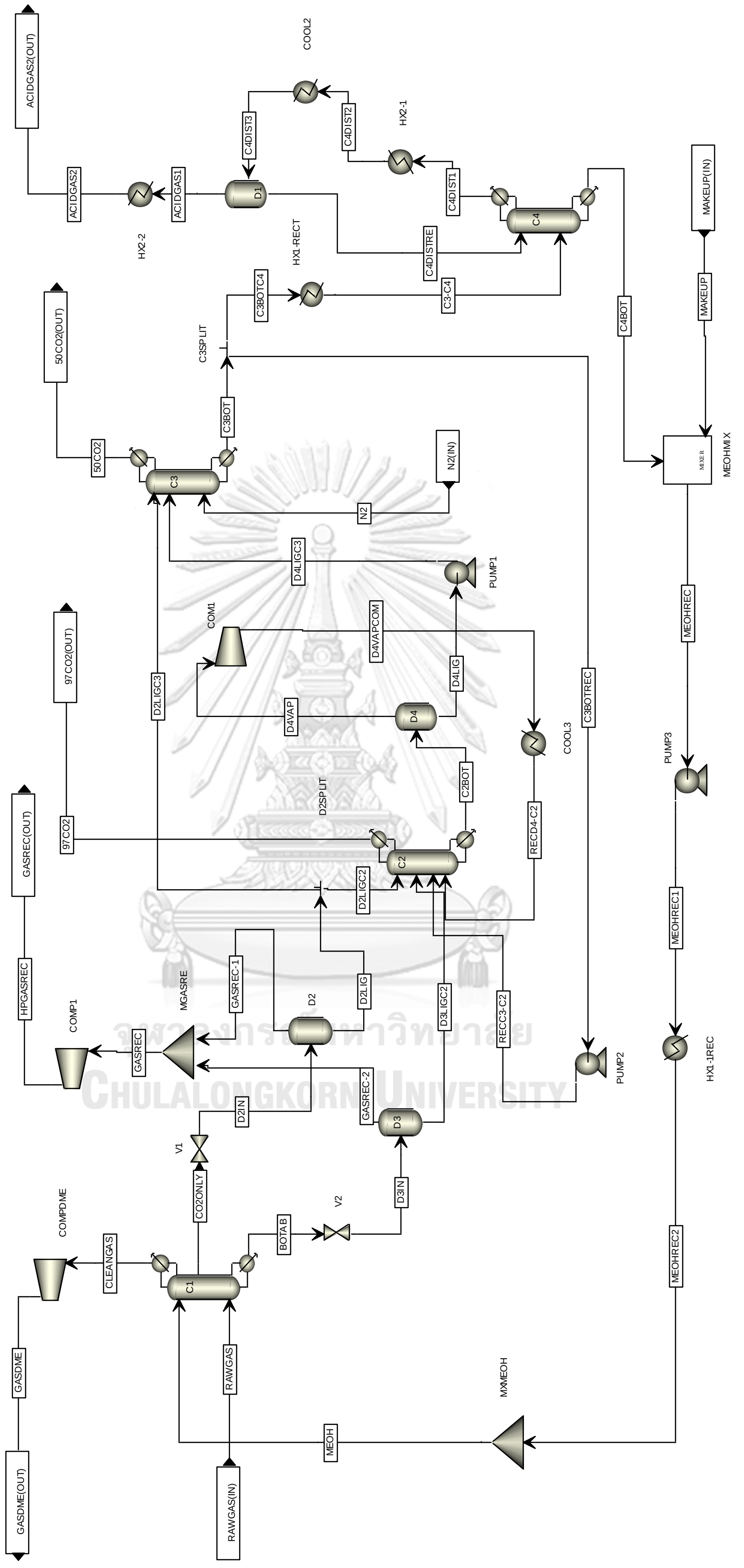


Figure D.3 Rectisol gas cleaner flow diagram

Table D.2 Stream table for Rectisol gas cleaner section

	Units	50CO2	97CO2	ACIDGAS2	BOTAB	C2BOT	C3BOT	C3BOTC4	C3BOTREC	C3-C4	C4BOT
Substream: ALL											
Mass Flow	KG/HR	264	218	394	4058	7233	7658	6433	1225	6433	6038
Temperature	C	-43	-33	1	-30	-39	-51	-51	-51	58	69
Pressure	BAR	2.0	3.0	1.2	32.0	3.0	2.0	2.0	2.0	2.0	1.2
Substream: MIXED											
Mass Flow	KG/HR	264	218	394	4058	7233	7658	6433	1225	6433	6038
Phase:		Vapor	Vapor	Vapor	Liquid	Liquid	Liquid	Liquid	Liquid	Mixed	Liquid
Vapor Fraction		1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0663	0.0000
Liquid Fraction		0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.9337	1.0000
Component Mass Fraction		1	1	1	1	1	1	1	1	1	1
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N2		0.4833	0.0018	0.0044	0.0001	0.0000	0.0003	0.0003	0.0003	0.0003	0.0000
H2		0.0001	0.0004	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CL2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0038	0.0170	0.0000	0.0034	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.5110	0.9752	0.9578	0.1465	0.1470	0.0586	0.0586	0.0586	0.0586	0.0000
SO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR		0.0004	0.0017	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2S		0.0000	0.0000	0.0236	0.0023	0.0019	0.0014	0.0014	0.0014	0.0014	0.0000
COS		0.0000	0.0000	0.0018	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001	0.0000
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4		0.0007	0.0030	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0006	0.0009	0.0125	0.8470	0.8509	0.9395	0.9395	0.9395	0.9395	1.0000

	Units	C4DIST1	C4DIST3	C4DISTRE	CLEANGAS	CO2ONLY	D2IN	D2LIGC2	D2LIGC3	D3IN
Substream: ALL										
Mass Flow	KG/HR	657	657	263	1379	2783	2783	1662	1108	4058
Temperature	C	50	-10	-10	-55	-42	-41	-41	-41	-30
Pressure	BAR	1.2	1.2	1.2	32.0	32.0	7.5	7.5	7.5	7.5
Substream: MIXED										
Mass Flow	KG/HR	6038	657	657	263	1379	2783	2770	1662	1108
Phase:		Liquid	Vapor	Mixed	Liquid	Vapor	Liquid	Liquid	Liquid	Liquid
Vapor Fraction		0.0000	1.0000	0.5261	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000

Liquid Fraction		1.0000	0.0000	0.4739	1.0000	0.0000	1.0000	1.0000	1.0000	1.0000
Component Mass Fraction		1	1	1	1	1	1	1	1	1
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N2		0.0000	0.0026	0.0026	0.0000	0.0208	0.0001	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0644	0.0001	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CL2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.8794	0.0036	0.0009	0.0009	0.0009
CO2		0.0000	0.5829	0.5829	0.0224	0.0009	0.0609	0.0598	0.0598	0.0595
SO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR		0.0000	0.0000	0.0000	0.0000	0.0233	0.0002	0.0001	0.0001	0.0001
H2S		0.0000	0.0150	0.0150	0.0022	0.0000	0.0000	0.0000	0.0000	0.0000
COS		0.0000	0.0012	0.0012	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4		0.0000	0.0000	0.0000	0.0000	0.0112	0.0003	0.0002	0.0002	0.0002
METHANOL		1.0000	0.3984	0.3984	0.9753	0.0001	0.9348	0.9390	0.9390	0.9392

	Units	D3IN	D3LIGC2	D4LIG	D4LIGC3	GASREC-1	GASREC-2	HPGASREC
From		V2	D3	D4	PUMP1	D2	D3	COMP1
To		D3	C2	PUMP1	C3	MGASRE	MGASRE	$C-27
Substream: ALL								
Mass Flow	KG/HR	657	657	657	263	1662	1108	4058
Temperature	C	50	57	-10	-10	-41	-41	-30
Pressure	BAR	1.2	1.2	1.2	1.2	7.5	7.5	7.5
Substream: MIXED								
Mass Flow	KG/HR	4058	4008	6684	6684	12	50	62
Phase:		Mixed	Liquid	Liquid	Liquid	Vapor	Vapor	Vapor
Vapor Fraction		0.0127	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000
Liquid Fraction		0.9873	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000
Component Mass Fraction		1	1	1	1	1	1	1
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N2		0.0001	0.0000	0.0000	0.0000	0.0117	0.0043	0.0058
H2		0.0001	0.0000	0.0000	0.0000	0.0277	0.0104	0.0139
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CL2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

NO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0034	0.0005	0.0000	0.0000	0.6053	0.2372	0.3110
CO2		0.1465	0.1393	0.0775	0.0775	0.3068	0.7239	0.6403
SO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR		0.0002	0.0001	0.0000	0.0000	0.0274	0.0112	0.0144
H2S		0.0023	0.0023	0.0017	0.0017	0.0000	0.0031	0.0025
COS		0.0002	0.0002	0.0001	0.0001	0.0000	0.0003	0.0002
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4		0.0002	0.0001	0.0000	0.0000	0.0207	0.0089	0.0113
METHANOL		0.8470	0.8575	0.9207	0.9207	0.0003	0.0006	0.0006

	Units	MAKEUP	MEOH	MEOHREC	N2	RAWGAS	RECC3-C2	RECD4-C2
Temperature	C		-55	69	20	-35	-51	-25
Pressure	BAR		32.3	1.2	2.0	32.6	3.0	3.0
Substream: MIXED								
Mass Flow	KG/HR	0	6038	6038	130	2181	1225	549
Phase:		Liquid	Liquid	Liquid	Vapor	Vapor	Liquid	Vapor
Vapor Fraction		0.0000	0.0000	0.0000	1.0000	1.0000	0.0000	1.0000
Liquid Fraction		1.0000	1.0000	1.0000	0.0000	0.0000	1.0000	0.0000
Component Mass Fraction		0	1	1	1	1	1	1
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N2		0.0000	0.0000	0.0000	1.0000	0.0133	0.0003	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0411	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CL2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.5668	0.0000	0.0001
CO2		0.0000	0.0000	0.0000	0.0000	0.3508	0.0586	0.9935
SO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR		0.0000	0.0000	0.0000	0.0000	0.0153	0.0000	0.0000
H2S		0.0000	0.0000	0.0000	0.0000	0.0043	0.0014	0.0053
COS		0.0000	0.0000	0.0000	0.0000	0.0003	0.0001	0.0004
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4		0.0000	0.0000	0.0000	0.0000	0.0078	0.0000	0.0001
METHANOL		0.0000	1.0000	1.0000	0.0000	0.0000	0.9395	0.0005

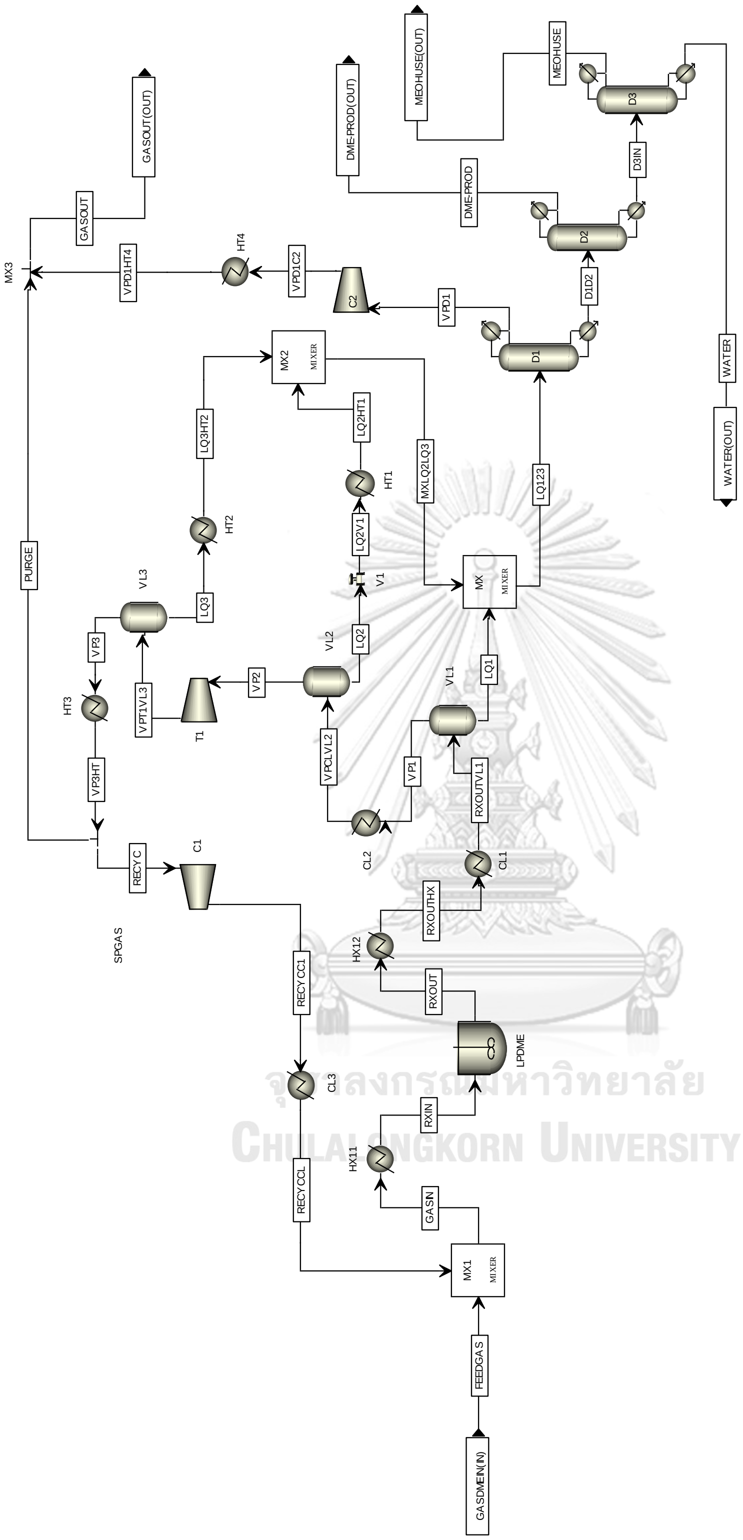


Figure D.4 DME production flow diagram

Table D.3 Stream table for DME synthesis section

	Units	D1D2	D2D3	D3IN	DME-PROD	FEEDGAS	GASOUT	LQ1	LQ123	LQ2	LQ2HT1
Substream: ALL											
Mass Flow	KG/HR	665	20	20	645	1379	725	14	1277	1018	1018
Temperature	C	90	176	176	44	100	23	40	13	-35	11
Pressure	BAR	25.0	10.0	10.0	10.0	66.4	27.7	60.6	27.7	58.8	27.7
Substream: MIXED											
Mass Flow	KG/HR	665	20	20	645	1379	725	14	1277	1018	1018
Phase:		Liquid	Liquid	Mixed	Vapor	Vapor	Vapor	Liquid	Mixed	Liquid	Mixed
Vapor Fraction		0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.0000	0.2263	0.0000	0.1888
Liquid Fraction		1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.7737	1.0000	0.8112
Component Mass Fraction		1	1	1	1	1	1	1	1	1	1
C		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0301	0.9942	0.9942	0.0000	0.0000	0.0000	0.8146	0.0157	0.0087	0.0087
N2		0.0000	0.0000	0.0000	0.0000	0.0208	0.0403	0.0003	0.0053	0.0058	0.0058
H2		0.0000	0.0000	0.0000	0.0000	0.0644	0.0033	0.0000	0.0002	0.0002	0.0002
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CL2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.8794	0.1099	0.0010	0.0213	0.0232	0.0232
CO2		0.0008	0.0000	0.0000	0.0008	0.0009	0.7792	0.0152	0.4275	0.3869	0.3869
SO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR		0.0000	0.0000	0.0000	0.0000	0.0233	0.0448	0.0003	0.0181	0.0186	0.0186
H2S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
COS		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4		0.0000	0.0000	0.0000	0.0000	0.0112	0.0218	0.0002	0.0072	0.0077	0.0077
METHANOL		0.0001	0.0026	0.0026	0.0000	0.0001	0.0000	0.0006	0.0000	0.0000	0.0000
DME		0.9690	0.0032	0.0032	0.9992	0.0000	0.0008	0.1677	0.5047	0.5487	0.5487

	Units	LQ3HT2	MEOHUSE	MXLQ2LQ3	PURGE	RECYC	RECYCC1	RECYCCL	RXIN	RXOUT
Substream: ALL										
Mass Flow	KG/HR	245	0	1263	114	3671	3671	3683	5062	5062
Temperature	C	11	9	12	25	25	133	77	240	260
Pressure	BAR	27.7	1.0	27.7	27.7	27.7	66.4	66.4	65.7	62.4
Substream: MIXED										
Mass Flow	KG/HR	245	0	1263	114	3671	3671	3683	5062	5062

Phase:		Mixed	Liquid	Mixed	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor
Vapor Fraction		0.3935	0.0000	0.2210	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Liquid Fraction		0.6065	1.0000	0.7790	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Component Mass Fraction		1	1	1	1	1	1	1	1	1
C		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.6337	0.0070	0.0000	0.0000	0.0000	0.0000	0.0000	0.0040
N2		0.0035	0.0000	0.0054	0.1976	0.1976	0.1976	0.1971	0.1491	0.1491
H2		0.0001	0.0000	0.0002	0.0190	0.0190	0.0190	0.0191	0.0314	0.0142
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CL2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0146	0.0000	0.0216	0.4624	0.4624	0.4624	0.4643	0.5773	0.3511
CO2		0.6185	0.0000	0.4319	0.1762	0.1762	0.1762	0.1750	0.1276	0.2396
SO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR		0.0173	0.0000	0.0183	0.0820	0.0820	0.0820	0.0819	0.0659	0.0659
H2S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
COS		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4		0.0053	0.0000	0.0073	0.0585	0.0585	0.0585	0.0584	0.0456	0.0456
METHANOL		0.0000	0.1624	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.3407	0.2039	0.5083	0.0043	0.0043	0.0043	0.0042	0.0031	0.1305

	Units	RXOUTVL1	VP2	VP3HT	VPCLVL2	VPD1	VPD1C2	VPD1HT4	VPT1VL3	WATER
Substream: ALL										
Mass Flow	KG/HR	5062	4030	3785	5048	612	612	612	4030	20
	Units	RXOUTVL1	VP2	VP3HT	VPCLVL2	VPD1	VPD1C2	VPD1HT4	VPT1VL3	WATER
Temperature	C	40	-35	25	-35	-19	-8	25	-63	100
Pressure	BAR	61.3	58.8	27.7	59.4	25.0	28.4	27.7	28.5	1.0
Substream: MIXED										
Mass Flow	KG/HR	5062	4030	3785	5048	612	612	612	4030	20
Phase:		Mixed	Vapor	Vapor	Mixed	Vapor	Vapor	Vapor	Mixed	Liquid
Vapor Fraction		0.9965	1.0000	1.0000	0.8760	1.0000	1.0000	1.0000	0.9664	0.0000
Liquid Fraction		0.0035	0.0000	0.0000	0.1240	0.0000	0.0000	0.0000	0.0336	1.0000
Component Mass Fraction		1	1	1	1	1	1	1	1	1
C		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0040	0.0000	0.0000	0.0018	0.0000	0.0000	0.0000	0.0000	1.0000
N2		0.1491	0.1858	0.1976	0.1495	0.0111	0.0111	0.0111	0.1858	0.0000

H2		0.0142	0.0178	0.0190	0.0143	0.0004	0.0004	0.0004	0.0178	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CL2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.3511	0.4351	0.4624	0.3521	0.0445	0.0445	0.0445	0.4351	0.0000
CO2		0.2396	0.2031	0.1762	0.2402	0.8911	0.8911	0.8911	0.2031	0.0000
SO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR		0.0659	0.0781	0.0820	0.0661	0.0379	0.0379	0.0379	0.0781	0.0000
H2S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
COS		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4		0.0456	0.0553	0.0585	0.0457	0.0150	0.0150	0.0150	0.0553	0.0000
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.1305	0.0247	0.0043	0.1304	0.0001	0.0001	0.0001	0.0247	0.0000

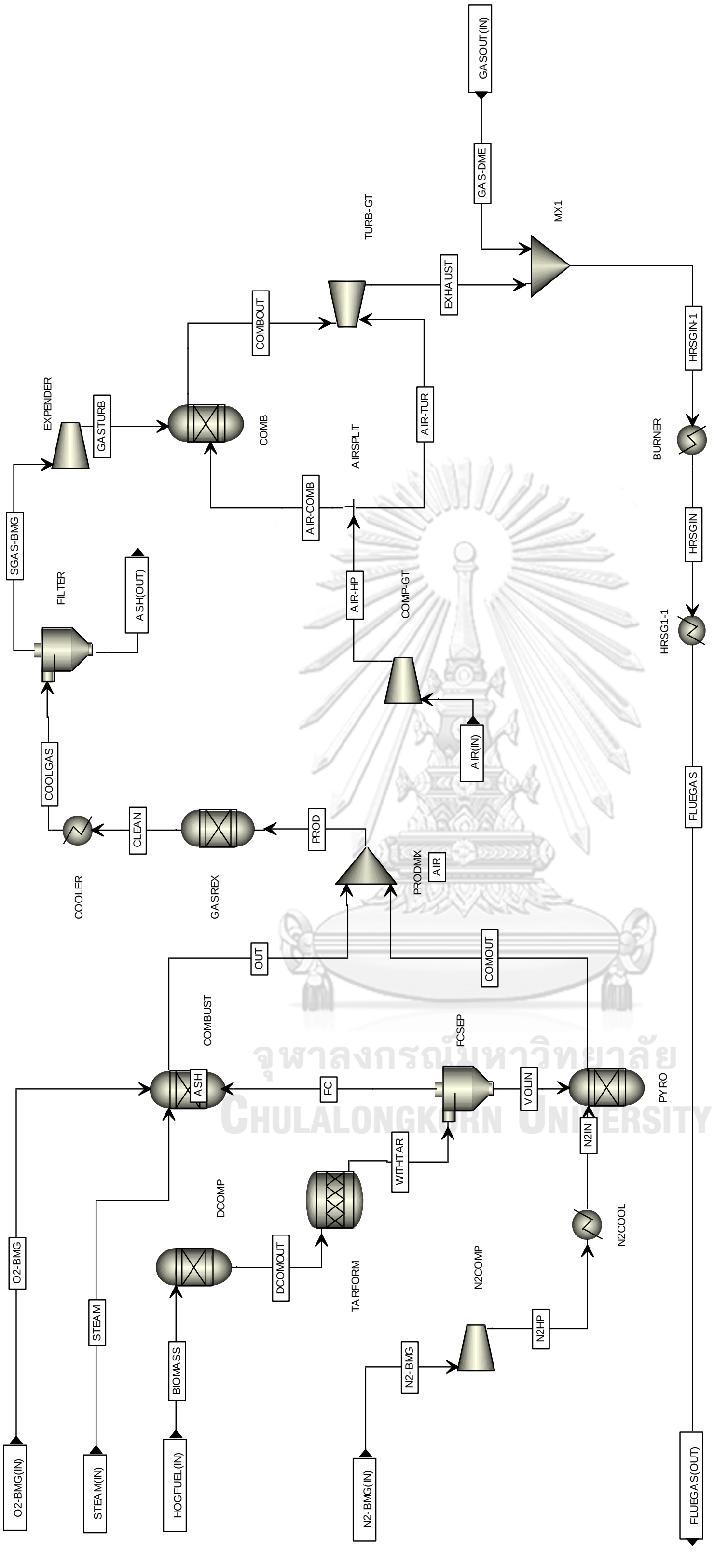


Figure D.5 Biomass gasification flow diagram

Table D.4 Stream table for biomass gasification section

	Units	AIR-COMB	AIR-HP	AIR-TUR	BIOMASS	CLEAN	COMBOUT	COMOUT	COOLGAS
Substream: ALL									
Mass Flow	KG/HR	76924	90074	13151	9831	16744	93439	9441	16744
Temperature	C	430	430	430	70	950	1357	500	421
Pressure	BAR	16.6	16.6	16.6	1.0	36.0	16.1	36.0	34.2
Mass vapor fraction		1.0000	1.0000	1.0000	0.0000	0.9863	1.0000	1.0000	0.9863
Mass solid fraction		0.0000	0.0000	0.0000	1.0000	0.0137	0.0000	0.0000	0.0137
Substream: MIXED									
Mass Flow	KG/HR	76924	90074	13151	0	16515	93439	9441	16515
Phase:		Vapor	Vapor	Vapor	Missing	Vapor	Vapor	Vapor	Vapor
Component Mass Fraction		1	1	1	0	1	1	1	1
C		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0000	0.0000		0.1972	0.0799	0.1118	0.1972
N2		0.7809	0.7809	0.7809		0.0506	0.5837	0.0829	0.0506
H2		0.0000	0.0000	0.0000		0.0266	0.0000	0.0023	0.0266
O2		0.2095	0.2095	0.2095		0.0000	0.0000	0.0000	0.0000
S		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
CL2		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000		0.0000	0.0909	0.0000	0.0000
NO2		0.0000	0.0000	0.0000		0.0000	0.0842	0.0000	0.0000
CO		0.0000	0.0000	0.0000		0.2249	0.0000	0.0136	0.2249
CO2		0.0004	0.0004	0.0004		0.4843	0.1521	0.5999	0.4843
SO		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
AR		0.0092	0.0092	0.0092		0.0087	0.0091	0.0000	0.0087
H2S		0.0000	0.0000	0.0000		0.0001	0.0000	0.0002	0.0001
COS		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
NH3		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
CH4		0.0000	0.0000	0.0000		0.0076	0.0000	0.1894	0.0076
METHANOL		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000
Substream: NCPSD									
Mass Flow	KG/HR	0	0	0	9831	229	0	0	229
Component Mass Fraction		0	0	0	1	1	0	0	1
BL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ASH		0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
HOGFUEL		0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000

	Units	DCOMOUT	DCOMOUT	FC	FLUEGAS	GAS-DME	GASTURB	HRSGIN	HRSGIN-1	N2IN

Substream: ALL										
Mass Flow	KG/HR	9831	9831	1159	107315	725	16515	107315	107315	768
Temperature	C	70	70	500	229	23	375	751	632	165
Pressure	BAR	1.0	1.0	36.0	1.0	27.7	24.0	1.0	1.1	37.7
Mass vapor fraction			0.5795	0.5795	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Mass solid fraction			0.4169	0.4169	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Substream: MIXED										
Mass Flow	KG/HR	8673	8673	0	107315	725	16515	107315	107315	768
Phase:		Mixed	Mixed	Missing	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor
Component Mass Fraction			1	1	1	1	1	1	1	1
C		0.3390	0.3390		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.2267	0.2267		0.0696	0.0000	0.1972	0.0696	0.0696	0.0000
N2		0.0016	0.0016		0.6042	0.0403	0.0506	0.6042	0.6042	1.0000
H2		0.0425	0.0425		0.0000	0.0033	0.0266	0.0000	0.0000	0.0000
O2		0.3900	0.3900		0.0257	0.0000	0.0000	0.0257	0.0257	0.0000
S		0.0002	0.0002		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CL2		0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000		0.0791	0.0000	0.0000	0.0791	0.0791	0.0000
NO2		0.0000	0.0000		0.0734	0.0000	0.0000	0.0734	0.0734	0.0000
CO		0.0000	0.0000		0.0007	0.1099	0.2249	0.0007	0.0007	0.0000
CO2		0.0000	0.0000		0.1377	0.7792	0.4843	0.1377	0.1377	0.0000
SO		0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR		0.0000	0.0000		0.0094	0.0448	0.0087	0.0094	0.0094	0.0000
H2S		0.0000	0.0000		0.0000	0.0000	0.0001	0.0000	0.0000	0.0000
COS		0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH3		0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4		0.0000	0.0000		0.0001	0.0218	0.0076	0.0001	0.0001	0.0000
METHANOL			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000		0.0000	0.0008	0.0000	0.0000	0.0000	0.0000
Substream: CIPSD										
Mass Flow	KG/HR	930	930	930	0	0	0	0	0	0
Component Mass Fraction			1	1	0	0	0	0	0	0
C		1.0000	1.0000	1.0000						
Substream: NCPSD										
Mass Flow	KG/HR	229	229	229	0	0	0	0	0	0
Component Mass Fraction			1	1	0	0	0	0	0	0
BL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ASH		1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HOGFUEL			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

	Units	O2-BMG	OUT	PROD	SGAS-BMG	STEAM	VOLIN	WITHTAR
Temperature	C	146	950	674	421	248	500	500
Pressure	BAR	36.0	36.0	36.0	34.2	38.0	36.0	36.0
Mass vapor fraction		1.0000	0.9687	0.9863	1.0000	1.0000	0.6611	0.5832
Mass solid fraction		0.0000	0.0313	0.0137	0.0000	0.0000	0.3389	0.4168
Substream: MIXED								
Mass Flow	KG/HR	3943	7074	16515	16515	2202	8673	8673
Phase:		Vapor	Vapor	Vapor	Vapor	Vapor	All	All
Component Mass Fraction		1	1	1	1	1	1	1
C		0.0000	0.0000	0.0000	0.0000	0.0000	0.3389	0.3389
H2O		0.0000	0.3112	0.1972	0.1972	1.0000	0.2267	0.2267
N2		0.0135	0.0075	0.0506	0.0506	0.0000	0.0016	0.0016
H2		0.0000	0.0000	0.0013	0.0266	0.0000	0.0425	0.0425
O2		0.9500	0.1794	0.0768	0.0000	0.0000	0.3900	0.3900
S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0002
CL2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0078	0.2249	0.0000	0.0000	0.0000
CO2		0.0000	0.4815	0.5492	0.4843	0.0000	0.0000	0.0000
SO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AR		0.0365	0.0203	0.0087	0.0087	0.0000	0.0000	0.0000
H2S		0.0000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0000
COS		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH4		0.0000	0.0000	0.1083	0.0076	0.0000	0.0000	0.0000
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Substream: CIPSD								
Mass Flow	KG/HR	0	0	0	0	0	0	930
Component Mass Fraction		0	0	0	0	0	0	1
C								1.0000
Substream: NCPSD								
Mass Flow	KG/HR	0	229	229	0	0	0	229
Component Mass Fraction		0	1	1	0	0	0	1
BL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ASH		0.0000	1.0000	1.0000	0.0000	0.0000	0.0000	1.0000
HOGFUEL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

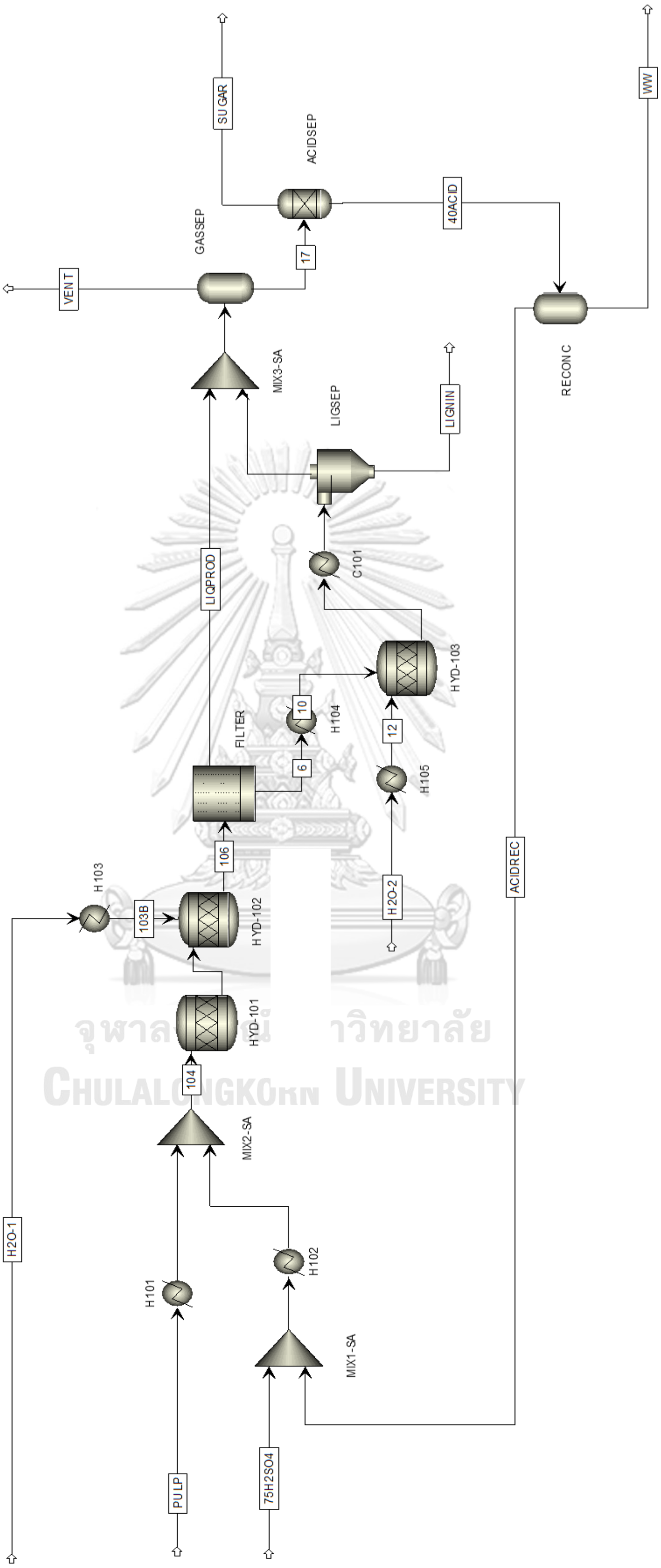


Figure D.6 Pulp hydrolysis process flow diagram

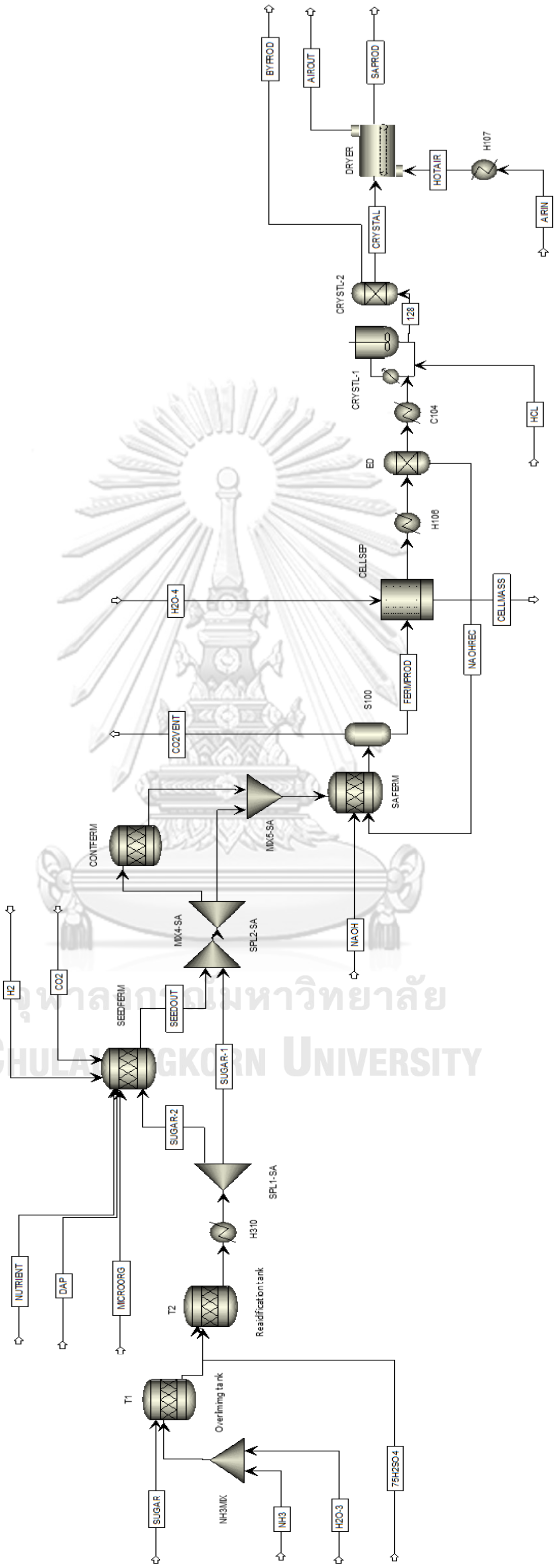


Figure D.7 Succinic acid production by fermentation

Table D.5 Stream table for succinic acid production

	Units	NH3	10	Pulp	101B	75H2SO4	102B	103A	103B	104	105
From			H104		H101		H102		H103	MIX2-SA	HYD-101
To		NH3MIX	HYD-103	H101	MIX2-SA	MIX1-SA	MIX2-SA	H103	HYD-102	HYD-101	HYD-102
Substream: ALL											
Mass Flow	KG/HR	108	4009	3688	3688	360	6474	10753	10753	10163	10163
Temperature	C	20	80	25	48	20	30	33	30	33	30
Pressure	BAR	9.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Substream: MIXED											
Mass Flow	KG/HR	108	344	16	16	360	6393	10753	10753	6408	6423
Phase:		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Vapor Fraction		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Liquid Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Component Mass Fraction		1	1	1	1	1	1	1	1	1	1
H2O		0.0700	0.6388	1.0000	1.0000	0.2500	0.0319	1.0000	1.0000	0.0343	0.0342
ETHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLUCOSE		0.0000	0.0393	0.0000	0.0000	0.0000	0.1056	0.0000	0.0000	0.1054	0.1051
GALACTOS		0.0000	0.0001	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0002	0.0002
MANNOSE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0001	0.0001
XYLOSE		0.0000	0.0118	0.0000	0.0000	0.0000	0.0316	0.0000	0.0000	0.0315	0.0314
ARABINOS		0.0000	0.0009	0.0000	0.0000	0.0000	0.0023	0.0000	0.0000	0.0023	0.0023
LGNSOL		0.0000	0.0011	0.0000	0.0000	0.0000	0.0020	0.0000	0.0000	0.0020	0.0029
HMF		0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0001	0.0001
FURFURAL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
AACID		0.0000	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0014
LACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
XYLITOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLYCEROL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SUCCACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH3		0.9300	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2SO4		0.0000	0.3075	0.0000	0.0000	0.7500	0.8262	0.0000	0.0000	0.8241	0.8223
Substream: CISOLID											
Mass Flow	KG/HR	0	3665	3673	3673	0	82	0	0	3754	3740
Component Mass Fraction		0	1	1	1	0	1	0	0	1	1
TAR			0.0000	0.0000	0.0000		0.0000			0.0000	0.0000
MICROOR			0.0000	0.0000	0.0000		0.0000			0.0000	0.0000
ASH			0.0137	0.0134	0.0134		0.0249			0.0136	0.0137
PROTEIN			0.0000	0.0000	0.0000		0.0000			0.0000	0.0000
ACETATE			0.0000	0.0024	0.0024		0.0000			0.0024	0.0000
LIGNIN			0.0294	0.0303	0.0303		0.0533			0.0308	0.0294
ARABINAN			0.0166	0.0165	0.0165		0.0161			0.0165	0.0166
XYLAN			0.2242	0.2234	0.2234		0.2183			0.2233	0.2242

MANNAN			0.0004	0.0004	0.0004		0.0004			0.0004	0.0004
GALACTAN			0.0020	0.0020	0.0020		0.0023			0.0020	0.0020
CELLULOS			0.7137	0.7115	0.7115		0.6847			0.7110	0.7137
SACRYS			0.0000	0.0000	0.0000		0.0000			0.0000	0.0000

	Units	107	SUGAR-2	11	110	111	112	113A	113B
From		H310	SPL1-SA	HYD-103					
To		SPL1-SA	SEEDFERM	C-101	SEEDFERM	SEEDFERM	SEEDFERM	SEEDFERM	SEEDFERM
Substream: ALL									
Mass Flow	KG/HR	30863	3086	14762	852	38	43	552	10754
Temperature	C	37	37	80	20	37	20	20	20
Pressure	BAR	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Substream: MIXED									
Mass Flow	KG/HR	30854	3085	14420	849	36	43	552	10754
Phase:		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Vapor	Vapor
Vapor Fraction		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Liquid Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000
Component Mass Fraction		1	1	1	1	1	1	1	1
H2O		0.8706	0.8706	0.7352	1.0000	0.6700	0.0000	0.0000	0.0000
ETHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLUCOSE		0.0877	0.0877	0.1924	0.0000	0.0000	0.0000	0.0000	0.0000
GALACTOS		0.0002	0.0002	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000
MANNOSE		0.0001	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
XYLOSE		0.0260	0.0260	0.0578	0.0000	0.0000	0.0000	0.0000	0.0000
ARABINOS		0.0019	0.0019	0.0043	0.0000	0.0000	0.0000	0.0000	0.0000
LGNSOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HMF		0.0001	0.0001	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000
FURFURAL		0.0008	0.0008	0.0021	0.0000	0.0000	0.0000	0.0000	0.0000
AACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
LACID		0.0000	0.0000	0.0000	0.0000	0.3300	0.0000	0.0000	0.0000
XYLITOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLYCEROL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SUCCACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2SO4		0.0000	0.0000	0.0073	0.0000	0.0000	0.0000	0.0000	0.0000
NH4SO4		0.0126	0.0126	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DAP		0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000
NANO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NAOH		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

CO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
C		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
FOMACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Substream: CISOLID									
Mass Flow	KG/HR	9	1	342	2	2	0	0	0
Component Mass Fraction		1	1	1	1	1	0	0	0
TAR		1.0000	1.0000	0.0001	0.0000	0.0000			
MICROOR		0.0000	0.0000	0.0000	1.0000	0.0000			
ASH		0.0000	0.0000	0.1469	0.0000	0.0000			
PROTEIN		0.0000	0.0000	0.0000	0.0000	1.0000			
ACETATE		0.0000	0.0000	0.0000	0.0000	0.0000			
LIGNIN		0.0000	0.0000	0.3149	0.0000	0.0000			
ARABINAN		0.0000	0.0000	0.0114	0.0000	0.0000			
XYLAN		0.0000	0.0000	0.1538	0.0000	0.0000			
MANNAN		0.0000	0.0000	0.0001	0.0000	0.0000			
GALACTAN		0.0000	0.0000	0.0056	0.0000	0.0000			
CELLULOS		0.0000	0.0000	0.3673	0.0000	0.0000			
SACRYS		0.0000	0.0000	0.0000	0.0000	0.0000			

	Units	SEEDOUT	116	117A	117B	118	NAOH	12	120F	CO2VENT
From		SEEDFERM	SPL2-SA	SPL2-SA	CONTFERM	MIX5-SA		H105	SAFERM	S100
To		MIX4-SA	MIX5-SA	CONTFERM	MIXIN	SAFERM	SAFERM	HYD-103	S100	
Substream: ALL										
Mass Flow	KG/HR	15325	41808	1293	1293	43101	38	10753	43260	17008
Temperature	C	37	30	30	33	30	50	80	37	37
Pressure	BAR	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Substream: MIXED										
Mass Flow	KG/HR	15309	41785	1292	1292	43077	38	10753	43236	17008
Phase:		Mixed	Mixed	Mixed	Mixed	Mixed	Liquid	Liquid	Mixed	Vapor
Vapor Fraction		0.9989	0.8076	0.8076	0.8103	0.8077	0.0000	0.0000	0.8191	1.0000
Liquid Fraction		0.0011	0.1924	0.1924	0.1897	0.1923	1.0000	1.0000	0.1809	0.0000
Component Mass Fraction		1	1	1	1	1	1	1	1	1
H2O		0.2327	0.6439	0.6439	0.6439	0.6439	0.0000	1.0000	0.6465	0.3612
ETHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLUCOSE		0.0170	0.0625	0.0625	0.0000	0.0607	0.0000	0.0000	0.0000	0.0000
GALACTOS		0.0000	0.0001	0.0001	0.0000	0.0001	0.0000	0.0000	0.0001	0.0000
MANNOSE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
XYLOSE		0.0050	0.0186	0.0186	0.0000	0.0180	0.0000	0.0000	0.0102	0.0000
ARABINOS		0.0004	0.0014	0.0014	0.0000	0.0013	0.0000	0.0000	0.0013	0.0000
LGNSOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HMF		0.0000	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000	0.0001	0.0000

FURFURAL		0.0002	0.0006	0.0006	0.0006	0.0006	0.0000	0.0000	0.0006	0.0009
AACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0131	0.0050
LACID		0.0008	0.0003	0.0003	0.0829	0.0028	0.0000	0.0000	0.0027	0.0000
XYLITOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLYCEROL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SUCCACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0622	0.0000
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2SO4		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH4SO4		0.0025	0.0090	0.0090	0.0090	0.0090	0.0000	0.0000	0.0090	0.0000
DAP		0.0028	0.0010	0.0010	0.0010	0.0010	0.0000	0.0000	0.0010	0.0000
NANO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NAOH		0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0037	0.0000
CO2		0.0361	0.0128	0.0128	0.0128	0.0128	0.0000	0.0000	0.0001	0.0002
H2		0.7025	0.2497	0.2497	0.2497	0.2497	0.0000	0.0000	0.2487	0.6321
C		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
FOMACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0008	0.0006
Substream: CISOLID										
Mass Flow	KG/HR	16	23	1	1	24	0	0	24	0
Component Mass Fraction		1	1	1	1	1	0	0	1	0
TAR		0.0550	0.3677	0.3677	0.3677	0.3677			0.3677	
MICROOR		0.8745	0.5850	0.5850	0.5850	0.5850			0.5850	
ASH		0.0000	0.0000	0.0000	0.0000	0.0000			0.0000	
PROTEIN		0.0706	0.0472	0.0472	0.0472	0.0472			0.0472	
ACETATE		0.0000	0.0000	0.0000	0.0000	0.0000			0.0000	
LIGNIN		0.0000	0.0000	0.0000	0.0000	0.0000			0.0000	
ARABINAN		0.0000	0.0000	0.0000	0.0000	0.0000			0.0000	
XYLAN		0.0000	0.0000	0.0000	0.0000	0.0000			0.0000	
MANNAN		0.0000	0.0000	0.0000	0.0000	0.0000			0.0000	
GALACTAN		0.0000	0.0000	0.0000	0.0000	0.0000			0.0000	
CELLULOS		0.0000	0.0000	0.0000	0.0000	0.0000			0.0000	
SACRYS		0.0000	0.0000	0.0000	0.0000	0.0000			0.0000	

	Units	H20-4	122L-B	122S	NAOHREC	126A	126B	HCL	128
From			H106	S505	ED	ED	C104		CRYSTL-1
To		CELLSEP	ED		SAFERM	C104	CRYSTL-1	CRYSTL-1	CRYSTL-2
Substream: ALL									
Mass Flow	KG/HR	3585	28322	1514	120	28202	28202	2	28203
Temperature	C	25	50	35	50	50	4	4	4
Pressure	BAR	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Substream: MIXED									
Mass Flow	KG/HR	3585	28322	1491	120	28201	28201	2	26443
Phase:		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Vapor	Liquid
Vapor Fraction		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000

Liquid Fraction		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	1.0000
Component Mass Fraction		1	1	1	1	1	1	0	1
H2O		1.0000	0.8518	0.8518	0.0000	0.8554	0.8554	0.0000	0.9123
ETHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLUCOSE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GALACTOS		0.0000	0.0002	0.0002	0.0000	0.0002	0.0002	0.0000	0.0002
MANNOSE		0.0000	0.0001	0.0001	0.0000	0.0001	0.0001	0.0000	0.0001
XYLOSE		0.0000	0.0148	0.0148	0.0000	0.0149	0.0149	0.0000	0.0159
ARABINOS		0.0000	0.0019	0.0019	0.0000	0.0019	0.0019	0.0000	0.0021
LGNSOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HMF		0.0000	0.0001	0.0001	0.0000	0.0001	0.0001	0.0000	0.0001
FURFURAL		0.0000	0.0003	0.0003	0.0000	0.0003	0.0003	0.0000	0.0003
AACID		0.0000	0.0161	0.0161	0.0000	0.0162	0.0162	0.0000	0.0173
LACID		0.0000	0.0040	0.0040	0.0000	0.0040	0.0040	0.0000	0.0043
XYLITOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLYCEROL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SUCCACID		0.0000	0.0901	0.0901	0.0000	0.0905	0.0905	0.0000	0.0300
NH3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2SO4		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH4SO4		0.0000	0.0130	0.0130	0.0000	0.0131	0.0131	0.0000	0.0139
DAP		0.0000	0.0014	0.0014	0.0000	0.0014	0.0014	0.0000	0.0015
NANO3		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NAOH		0.0000	0.0053	0.0053	1.0000	0.0011	0.0011	0.0000	0.0011
FOMACID		0.0000	0.0008	0.0008	0.0000	0.0008	0.0008	0.0000	0.0008
Substream: CISOLID									
Mass Flow	KG/HR	0	0	23	0	0	0	0	1760
Component Mass Fraction		0	1	1	0	1	1	0	1
TAR			0.3677	0.3677		0.3677	0.3677		0.0001
MICROOR			0.5850	0.5850		0.5850	0.5850		0.0002
ASH			0.0000	0.0000		0.0000	0.0000		0.0000
PROTEIN			0.0472	0.0472		0.0472	0.0472		0.0000
ACETATE			0.0000	0.0000		0.0000	0.0000		0.0000
LIGNIN			0.0000	0.0000		0.0000	0.0000		0.0000
ARABINAN			0.0000	0.0000		0.0000	0.0000		0.0000
XYLAN			0.0000	0.0000		0.0000	0.0000		0.0000
MANNAN			0.0000	0.0000		0.0000	0.0000		0.0000
GALACTAN			0.0000	0.0000		0.0000	0.0000		0.0000
CELLULOS			0.0000	0.0000		0.0000	0.0000		0.0000
SACRYS			0.0000	0.0000		0.0000	0.0000		0.9997

	Units	SUGAR	40ACID	2	20	ACIDREC	75H2SO4
From		ACIDSEP	ACIDSEP	T1	RECONC	RECONC	
To		T1	RECONC	T2		MIX1-SA	T2

Substream: ALL							
Mass Flow	KG/HR	9003	22043	30619	15928	6114	244
Temperature	C	28	28	29	180	180	20
Pressure	BAR	1.0	1.0	1.0	1.0	1.0	1.0
Substream: MIXED							
Mass Flow	KG/HR	9003	21961	30610	15928	6033	244
Phase:		Liquid	Liquid	Liquid	Vapor	Liquid	Liquid
Vapor Fraction		0.0000	0.0000	0.0000	1.0000	0.0000	0.0000
Liquid Fraction		1.0000	1.0000	1.0000	0.0000	1.0000	1.0000
Component Mass Fraction		1	1	1	1	1	1
H2O		0.5871	0.7221	0.8756	0.9884	0.0189	0.2500
ETHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLUCOSE		0.3004	0.0308	0.0884	0.0001	0.1119	0.0000
GALACTOS		0.0006	0.0001	0.0002	0.0000	0.0002	0.0000
MANNOSE		0.0002	0.0000	0.0001	0.0000	0.0001	0.0000
XYLOSE		0.0901	0.0092	0.0262	0.0001	0.0335	0.0000
ARABINOS		0.0067	0.0007	0.0019	0.0000	0.0025	0.0000
LGNSOL		0.0000	0.0008	0.0000	0.0004	0.0021	0.0000
HMF		0.0004	0.0000	0.0001	0.0000	0.0001	0.0000
FURFURAL		0.0027	0.0003	0.0008	0.0004	0.0000	0.0000
AACID		0.0000	0.0004	0.0000	0.0006	0.0000	0.0000
LACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
XYLITOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GLYCEROL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SUCCACID		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NH3		0.0000	0.0000	0.0021	0.0000	0.0000	0.0000
H2SO4		0.0117	0.2356	0.0000	0.0102	0.8307	0.7500
NH4SO4		0.0000	0.0000	0.0046	0.0000	0.0000	0.0000
Substream: CISOLID							
Mass Flow	KG/HR	0	82	9	0	82	0
Component Mass Fraction		0	1	1	0	1	0
TAR			0.0000	1.0000		0.0000	
MICROOR			0.0000	0.0000		0.0000	
ASH			0.0249	0.0000		0.0249	
ACETATE			0.0000	0.0000		0.0000	
LIGNIN			0.0533	0.0000		0.0533	
ARABINAN			0.0161	0.0000		0.0161	
XYLAN			0.2183	0.0000		0.2183	
MANNAN			0.0004	0.0000		0.0004	
GALACTAN			0.0023	0.0000		0.0023	
CELLULOS			0.6847	0.0000		0.6847	

	Units	H20-3	5	6	7	LIQPROD
From			NH3MIX	FILTER	C-101	FILTER
To		NH3MIX	T2	H104	LIGSEP	MIX3-SA
Substream: ALL						
Mass Flow	KG/HR	21509	21616	4009	14762	16907
Temperature	C	25	28	30	25	30
Pressure	BAR	1.0	1.0	1.0	1.0	1.0
Substream: MIXED						
Mass Flow	KG/HR	21509	21616	344	14420	16833
Phase:		Liquid	Liquid	Liquid	Liquid	Liquid
Vapor Fraction		0.0000	0.0000	0.0000	0.0000	0.0000
Liquid Fraction		1.0000	1.0000	1.0000	1.0000	1.0000
Component Mass Fraction		1	1	1	1	1
H2O		1.0000	0.9954	0.6388	0.7352	0.6388
ETHANOL		0.0000	0.0000	0.0000	0.0000	0.0000
GLUCOSE		0.0000	0.0000	0.0393	0.1924	0.0393
GALACTOS		0.0000	0.0000	0.0001	0.0004	0.0001
MANNOSE		0.0000	0.0000	0.0000	0.0001	0.0000
XYLOSE		0.0000	0.0000	0.0118	0.0578	0.0118
ARABINOS		0.0000	0.0000	0.0009	0.0043	0.0009
LGNSOL		0.0000	0.0000	0.0011	0.0000	0.0011
HMF		0.0000	0.0000	0.0000	0.0003	0.0000
FURFURAL		0.0000	0.0000	0.0000	0.0021	0.0000
AACID		0.0000	0.0000	0.0005	0.0000	0.0005
NH3		0.0000	0.0046	0.0000	0.0000	0.0000
H2SO4		0.0000	0.0000	0.3075	0.0073	0.3075
NH4SO4		0.0000	0.0000	0.0000	0.0000	0.0000
Substream: CISOLID						
Mass Flow	KG/HR	0	0	3665	342	75
Component Mass Fraction		0	0	1	1	1
TAR				0.0000	0.0001	0.0000
ASH				0.0137	0.1469	0.0137
PROTEIN				0.0000	0.0000	0.0000
ACETATE				0.0000	0.0000	0.0000
LIGNIN				0.0294	0.3149	0.0294
ARABINAN				0.0166	0.0114	0.0166
XYLAN				0.2242	0.1538	0.2242
MANNAN				0.0004	0.0001	0.0004
GALACTAN				0.0020	0.0056	0.0020
CELLULOS				0.7137	0.3673	0.7137
SACRYS				0.0000	0.0000	0.0000

Appendix E: Stream table from process simulation of integrated biorefinery in Kraft pulping process

Table E.1 Stream table for gasification-based biorefinery

Gasification-based biorefinery						
Stream		Raw gas	Clean gas	RXIN	RXOUT	DME
Mass Flow	KG/HR	3366	1376	3045	3045	711
Temperature	C	-35	-58.3	240	260	44.5
Pressure	BAR	32.6	32	65.7	62.4	10
Component Mass Fraction						
H2O		0.0000	0.0000	0.0000	0.0320	0.0000
N2		0.0040	0.0097	0.1095	0.1095	0.0000
H2		0.0324	0.0784	0.0624	0.0279	0.0000
CO		0.3520	0.8423	0.4260	0.0479	0.0000
CO2		0.5580	0.0064	0.1279	0.2729	0.0006
AR		0.0159	0.0372	0.1377	0.1377	0.0000
H2S		0.0245	0.0000	0.0000	0.0000	0.0000
COS		0.0015	0.0000	0.0000	0.0000	0.0000
CH4		0.0116	0.0259	0.1318	0.1318	0.0000
METHANOL		0.0001	0.0000	0.0000	0.0022	0.0000
DME		0.0000	0.0000	0.0046	0.2381	0.9994

Table E.2 Stream table for succinic acid production

Succinic acid production					
Stream		Pulp	Sugars	Ferm out	SA
Mass Flow	KG/HR	4089	31217	28629	2136
Temperature	C	25	37	4	4
Pressure	BAR	1.01	1.01	1.01	1.01
Liquid&Vapor	KG/HR	23	31212	28628	0
Component Mass Fraction					
H2O		1.0000	0.8605	0.8442	0.0000
ETHANOL		0.0000	0.0000	0.0000	0.0000
GLUCOSE		0.0000	0.1094	0.0000	0.0000
GALACTOS		0.0000	0.0002	0.0002	0.0000
MANNOSE		0.0000	0.0042	0.0042	0.0000
XYLOSE		0.0000	0.0114	0.0065	0.0000
ARABINOS		0.0000	0.0013	0.0013	0.0000
HMF		0.0000	0.0002	0.0002	0.0000
FURFURAL		0.0000	0.0004	0.0001	0.0000
AACID		0.0000	0.0000	0.0202	0.0000
LACID		0.0000	0.0000	0.0043	0.0000
SUCCACID		0.0000	0.0000	0.1024	0.0000
H2SO4		0.0000	0.0000	0.0000	0.0000
NH4SO4		0.0000	0.0124	0.0129	0.0000
DAP		0.0000	0.0000	0.0014	0.0000
NAOH		0.0000	0.0000	0.0011	0.0000
CO2		0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000
FOMACID		0.0000	0.0000	0.0010	0.0000

Solid	KG/HR	4065	5	0	2136
Component Mass Fraction					
TAR		0.0000	1.0000	0.2534	0.0000
MICROOR		0.0000	0.0000	0.6958	0.0000
ASH		0.0057	0.0000	0.0000	0.0000
PROTEIN		0.0000	0.0000	0.0508	0.0000
ACETATE		0.0101	0.0000	0.0000	0.0000
LIGNIN		0.0403	0.0000	0.0000	0.0000
ARABINAN		0.0102	0.0000	0.0000	0.0000
XYLAN		0.0895	0.0000	0.0000	0.0000
MANNAN		0.0302	0.0000	0.0000	0.0000
GALACTAN		0.0024	0.0000	0.0000	0.0000
CELLULOS		0.8115	0.0000	0.0000	0.0000
SACRYS		0.0000	0.0000	0.0000	1.0000

VITA

NAME	Ghochapon Mongkhonsiri
DATE OF BIRTH	6 April 1992
PLACE OF BIRTH	Udonthani, Thailand
INSTITUTIONS ATTENDED	Udonpittayanukoon School in sciences and mathematics program King Mongkut's University of Technology Thonburi for bachelor's degree in chemical engineering
HOME ADDRESS	112/54 Moo 8, Thahan Road, Mak Khaeng Sub-district, Mueang Udon Thani District, Udon Thani 41000
PUBLICATION	1.Ghochapon Mongkhonsiri, Rafiqul Gani, Pomthong Malakul, Suttichai Assabumrungrat. 2018. Integration of the Biorefinery Concept for the Development of Sustainable Processes for Pulp and Paper Industry. Computers and Chemical Engineering. 119 : 70-84. 2. Ghochapon Mongkhonsiri, Pongtorn Charoensuppanimit , Amata Anantpinijwatna, Rafiqul Gani, Suttichai Assabumrungrat. 2020. Process development of sustainable biorefinery system integrated into the existing pulping process. Journal of Cleaner Production. 255 : 120278
AWARD RECEIVED	First-class honors in bachelor's degree of chemical engineering The gold medal of basketball in high-school sport event Completion of Kumon mathematics programme