Computers and Chemical Engineering 119 (2018) 70–84

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Integration of the biorefinery concept for the development of sustainable processes for pulp and paper industry

Ghochapon Mongkhonsiri[a], Rafiqul Gani[b], Pomthong Malakul[c], Suttichai Assabumrungrat[a,*]

[a] Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[b] PSE for SPEED, Skyttemosen 6, Allerod DK 3450, Denmark
[c] Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand

ARTICLE INFO

Article history:
Received 24 May 2018
Revised 5 July 2018
Accepted 19 July 2018
Available online 24 August 2018

Keywords:
Pulp and paper industry
Biorefinery
Process integration
Process synthesis
Superstructure optimization

ABSTRACT

This work aims at developing sustainable processes for pulp and paper industry by integration of the biorefinery concept to an existing pulp and paper process. A systematic methodology employing a superstructure-based process synthesis approach is employed with support from computer-aided tools to determine potential pathways for a long-term sustainable growth objective. A superstructure of the multi-product biorefinery process network for the pulp and paper industry is developed. It is divided into three sub-networks, a chemical pulping section, a biochemical production section and a black liquor utilization section. Superstructure optimization is performed with the objective to maximize profit to determine optimal integrated networks for three scenarios. The obtained results provide useful insights for further development of the optimal networks as sustainable integrated biorefinery combined with pulp and paper mills.

1. Introduction

The immense consumption of fossil fuel has contributed to significant increases in greenhouse gas emissions and depleted petroleum resource reserves. Many reasons have driven the interest in seeking sustainable and renewable alternatives to replace fossil fuels for industrial and domestic consumptions (Yuan et al., 2013). Biorefinery, especially "Lignocellulosic Biorefinery" that is a non-food feedstock based process, is considered as a key in achieving a sustainable society where energy, chemicals and materials are less fuel dependent contributing to addressing the climate change problem. 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 synthesis and design method plays an important role in the search for a sustainable process network for production of biofuels, biochemicals and biomaterials that also considers economical, environmental and societal issues.

The pulp and paper industry today represents the world's largest woody biomass utilization system and is a large user and producer of bioenergy and biomaterials. Nowaday, Kraft and Soda processes are the most widely used pulping technologies. The Kraft process with a chemical recovery system is dominant for hardwood feedstock. It entails chemical treatment of wood chips with a mixture of sodium hydroxide and sodium sulfide to degrade the linkage of lignin, hemicelluloses and cellulose, and then cellulose fiber is separated as pulp. The spent pulping chemical is recovered by a chemical recovery technology for reuse in the wood digestion unit. Besides wood, agricultural residues, e.g. bagasse, rice straw and corn stover, have been used as raw materials supplementing the production in pulp and paper industry. The Soda process with sodium hydroxide as a fiber digestion agent without using sodium sulfide has been mostly applied in the non-wood pulping technology using agricultural residues as raw material due to several good points involving high yield at low temperature, good pulp properties and the obtaining of sulfur-free products (Iglesias et al., 1996). For Soda processs, sodium hydroxide can be recovered by the chemical recovery technique similar to that used in the Kraft process. The pulp and paper production technology has evolved for a long time, the current pulp and paper production is characterized by low efficiency of raw material and energy utilization, low innovative development, high investment and high price volatility (Pätäri et al., 2016). Moreover, the printing paper consumption has been diminishing because of increased use of digital

* Corresponding author.
E-mail address: Suttichai.A@chula.ac.th (S. Assabumrungrat).

https://doi.org/10.1016/j.compchemeng.2018.07.019
0098-1354/

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

media through computers, tablets and smart phones. It has been predicted that paper may not become necessary anymore for publication purposes. The traditional pulp and paper industry needs to transform to respond to the current situation, increased competition and changes in consumption habits. The key challenge of future pulp and paper industry is to materialize a transformation towards a low-carbon bioeconomy as well as incorporate the necessary green innovations.

Integrated biorefinery into an existing pulp mill has been determined as a potential pathway for a long-term sustainable growth of not only pulp and paper industry but also biorefinery. To achieve the goal of improvement of efficiency and profitability, evaluation of opportunities for generation of new revenues from new value-added products within an existing infrastructure of the pulp mill has attracted much attention. The typical pulping process utilizes lignocellulose biomass, including cellulose, hemicellulose and lignin, fossil fuel, chemicals and water to produce paper pulp, mostly composing of cellulose, steam and power. However, an integrated biorefinery could transform a low profit margin paper manufacturing production into a marketable multiple bioproduct production system with sharing of raw materials, by-products, utilities, and infrastructure with the existing pulp mill. Rafione, Marinova, Montastruc, and Paris (2014) proposed a green integrated forest biorefinery (GIFBR) concept. A pulp mill as the core of the complex is integrated with a biorefinery unit to produce value-added bioproducts for generating a new revenue stream, a woody biomass gasification plant to produce syngas for fossil fuel substitution and a polygeneration unit to generate green power for supply to the integrated facility. The integrated complex could operate under energy self-sufficiency. Moreover, the concept aims to obtain a zero-fossil fuel consumption, minimum fresh water and energy demand, reduced amounts of water effluents and greenhouse gases emissions. To be technically and economically feasible, the GIFBR concept suggested that the development of integrated facilities is performed phase by phase to spread investment cost overtime and mitigate the risks. They also proposed a step by step methodology for synthesis of a biorefinery network (Rafione et al., 2014).

Paper pulp is a cellulosic fiber that is extracted from lignocellulosic biomass. The lignocellulosic biorefinery is well known in two platforms, i.e. biochemical platform and thermochemical platform. The study of lignocellulosic biorefinery has strongly influenced the development of biofuels and biochemicals production from cellulose and hemicellulose via hydrolysis and fermentation, called the biochemical platform (Menon and Rao, 2012). It is mainly based on sugars which can be derived from fermentation or other biological processing of biomass. Different types of sugar are further converted into various fuels and chemicals. When paper demand would be diminished, pulp, cellulose-rich material, as well as biomass residue from pulp mill such as wood bark and bagasse pith could be used as feedstock for biofuel and biochemical production. Pre-extracted hemicellulose before pulping process has also attracted attention as feedstock for biochemical production such as ethanol (Huang et al., 2010), furfural (Montastruc et al., 2011) or others. However, pre-extraction directly decreases pulp yield and paper properties (Walton et al., 2010). Extraction of hemicelluloses from wood prior to pulping process is currently in practice commercially in the production of dissolving pulp, a high purity cellulose pulp, for processing into cellulose derivatives, for example, cellulose nitrate, cellulose xanthate (rayon fibers), and cellulose acetate (Mateos-Espejel et al., 2011; Rafione et al., 2014). The challenge of hemicellulose utilization for pulp and paper industry is the design of technology strategies for hemicellulose extraction while maintaining product quality.

For the thermochemical platform, biomass is converted to synthesis gas (hydrogen and carbon monoxide) or pyrolysis oil via gasification or pyrolysis, respectively. The thermochemical platform applied to chemical pulping process mainly consists of gasification of black liquor and biomass residue, and lignin extraction from black liquor (Bajpai, 2013). Gasification of black liquor has gone through a step-wise development since the 1960s, now it is designated as an alternative chemical recovery technology for conventional boiler replacement (IEA Biorefinery, 2007). The sulfur-free synthesis gas (syngas) consisting of mostly carbon monoxide, hydrogen and carbon dioxide is the gas product from gasification plant. The utilization of syngas occurs mainly via two routes; black liquor gasification combined cycle (BLGCC) and black liquor gasification with motor fuels production (BLGMF). In BLGCC, a gas turbine is applied to use the syngas for power generation. It can increase the potential to generate power and diminish the heat surplus of the mill. While, BLGMF is an alterative pathway to produce bio-fuels such as motor fuels, Fischer–Tropsch liquids (FTL), dimethyl ether (DME), methanol, and mixed-alcohol

(MA), a mixture of ethanol and higher alcohols, substituting fossil fuels (Isaksson et al., 2016). Also, biomass gasification could be integrated in pulp and paper industry due to economic and environmental advantages rather than conventional combustion (Consonni et al., 2009). It does not only supply the energy necessary for the process but also produces valuable chemicals.

In pulp and paper industries, most lignin is separated from raw material into black liquor. Extraction of lignin from the black liquor has been of interest for improvement of economy of the pulp and paper industry. Lignin is a promising renewable raw material for biorefinery. The extracted lignin can subsequently be a high heating value biofuel as an alternative fuel for the pulp and paper mill. Moreover, it has potential for additional conversion to produce biochemicals especially aromatic hydrocarbons, bio-oil via the cracking of lignin at near critical conditions, and bio-materials such as activated carbon and carbon fiber (Ragauskas et al., 2014). Generally, recovery boiler capacity is a bottleneck of pulp productivity, the separation of lignin from black liquor before feeding to a recovery boiler unit can enhance the annual tons of pulp production because off-loading of the recovery boiler permits an increase in black liquor throughput to obtain an increase in pulp production (Lourençon et al., 2015). The LignoBoost process (Tomani, 2010), a commercial process for high quality lignin precipitation at low cost, offers opportunities for efficient extraction of lignin.

Cost-effective biorefinery synthesis and design strategies and effective evaluation tools play a key role for development of practical and sustainable integrated biorefinery network for the pulp and paper industry. The selection of biorefinery technology for implementation depends on several factors such as processing condition, local market supply chains, raw material product price, price of utility and fuels, possible mass and energy integration. A systematic hierarchical methodology should be suitable for addressing all these factors in a step-wise manner (Babi et al., 2015). Superstructure-based systematic methodology provides the overview and analysis needed for commercial development of biorefinery integrated with pulping processes. The superstructure represents all possible pathways in an integrated network of processing options. Superstructure optimization can be performed to determine the most effective pathways in terms of defined performance criteria (Zondervan et al., 2011).

This study aims to identify 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.

2. Synthesis Methodology

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 paper, the stepwise approach consisting of four steps, as shown in Fig. 1 is considered.

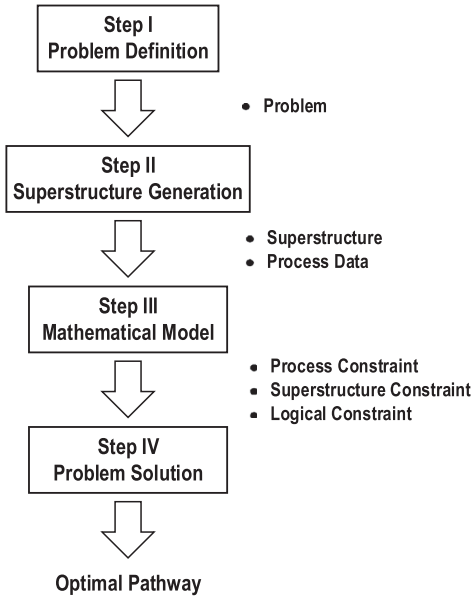

Fig. 1. Workflow of superstructure-based process synthesis methodology.

2.1. Step 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 Eq. (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.

2.2. Step 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 Fig. 2 (Quaglia et al., 2013). Each processing step consists of associated intervals. The model representing a process interval in the superstructure as shown in Fig. 3 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 in-

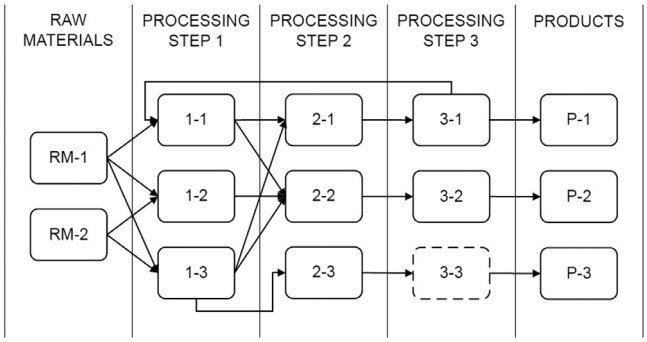

Fig. 2. Generic superstructure for a synthesis problem of processing networks illustrating the concepts of processing step (column), processing interval (box), by-pass (box with dotted outline), primary connection (arrow starting from the right hand side of the interval), secondary connection (arrow starting from the top or bottom of the interval) (Bertran et al., 2017).

formation 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.

2.3. Step 3: Mathematical model

A set of mathematical models is developed and validated to represent the superstructure. The generic modeling approach that has proposed in several case studies in process synthesis problems (Frauzem et al., 2015, Rizwan et al., 2013, Zondervan et al., 2011) 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 Fig. 4. 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 Eqs. (2)–(22) (Quaglia et al., 2015). 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).

Mathematical model of superstructure optimization

Objective function

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

Process interval equation

$$\text{Chemical added } g_{i,kk}^M = \sum_{ii} \mu_{i,ii,kk} f_{i,k}^{IN} \quad (2)$$

$$\text{Reaction } f_{i,kk}^R = f_{i,kk}^M + \sum_{rr,react} f_{react,kk}^M \theta_{react,kk,rr} \cdot \frac{\gamma_{i,kk,rr}}{\gamma_{i,kk,rr}} \cdot \frac{MW_i}{MW_{react}} \quad (3)$$

$$\text{Waste separation } f_{i,kk}^W = f_{i,kk}^R \left(1 - \delta_{i,kk}\right) \quad (4)$$

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

$$\text{Utility consumption } g_{j,kk}^U = g_{j,kk}^{U,1} + g_{j,kk}^{U,2} + g_{j,kk}^{U,3} \quad (6)$$

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

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

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

$$\text{Product separation } f_{i,kk}^{OUT,P} = f_{i,kk}^W \sigma_{i,kk} \quad (10)$$

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

$$\text{Capital cost } invl_{kk} = f\left(f_{i,kk}^W\right) \quad (12)$$

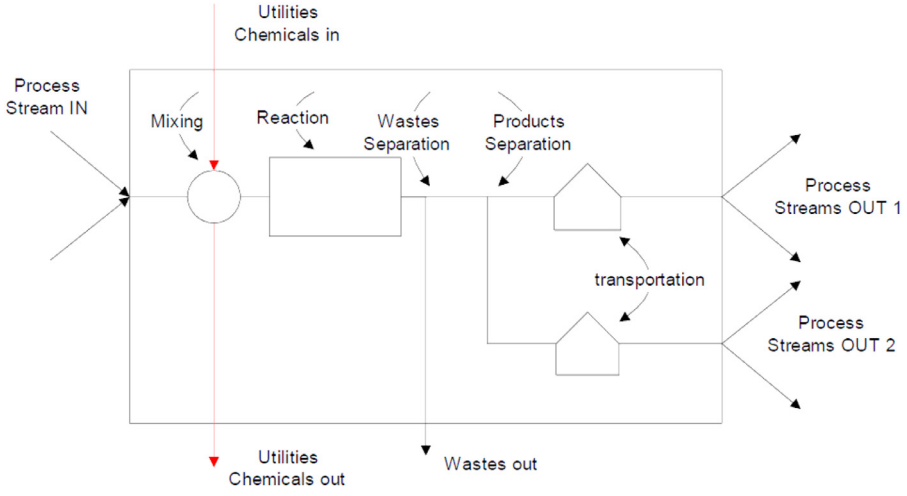

Fig. 3. Generic model of a process interval (Kongpanna et al., 2016).

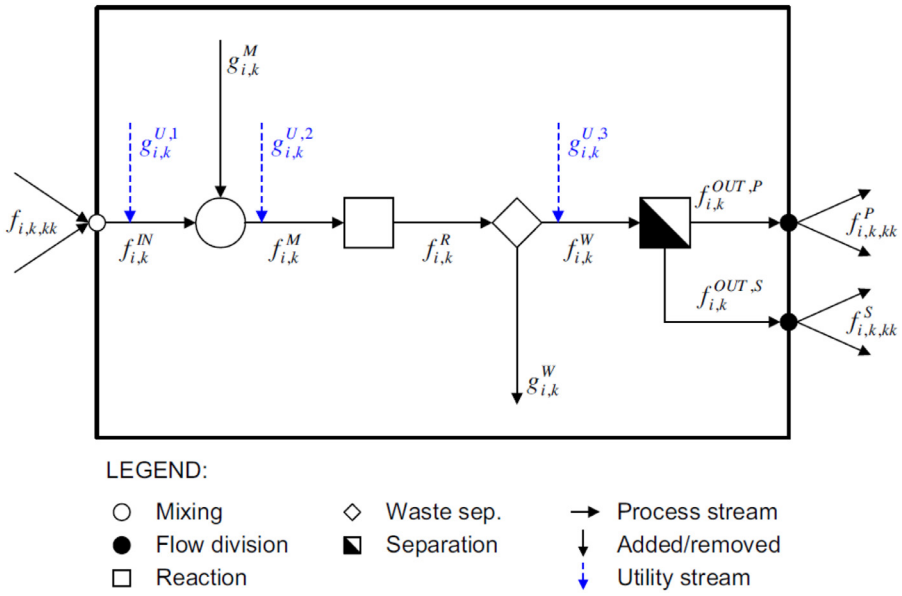

Fig. 4. The generic process interval with internal variables (Bertran et al., 2017).

Superstructure flow model

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

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

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

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

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

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

Superstructure logical constraint

$$\sum_{kk} y_{kk} V_{kk,step} \le 1 \tag{19}$$

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

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

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

2.4. Step 4: Problem solution

The optimization problem with the formulated MILP or MINLP models from step 3 aresolved with GAMS (GAMS Development Corporation, 2013) 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.

3. Results and discussion

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. Next, results from the superstructure optimization are given and analyzed for the three scenarios to determine optimal networks. The first scenario considers the alternatives of pulp pathway for paper production or for feedstock of biochemical production. The second scenario considers biochemical co-production with pulp for paper production. Here different percentages of pulp for paper production are specified and the rest of unbleached pulp is fed to the biochemical production section. In the third scenario, multiple biochemical production integrated with pulping process is considered. Optimal networks for each scenario are compared with stand-alone pulping process and other pathways.

3.1. 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.

3.1.1. 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, 2016). 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 economical 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 pulpingprocesses 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.

3.1.2. 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.

3.1.2.1. 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).

3.1.2.2. 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).

3.1.2.3. 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, Domine, Parvulescu, and Petru, 2015). It has been expected for the market size to grow to about 699,449 MT in 2020 (Weastra, 2012). 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 et al., 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, 2012). 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, Rumler, and Jain, 1999), *Mannheimia succiniciproducens* (Lee, Lee, Hong, and Chang, 2002), *Corynebacterium glutamicum* (Okino et al., 2005), *Anaerobiospirillum succiniciproducens* (Lee, Lee, Hong, Chang, and Park, 2003) and *Escherichia coli* (Donnelly et al., 1998). 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, Jain, and Soni, 1998), reactive ex-

traction (Glassner, Elankovan, Beacom, and Berglund, 1995), direct vacuum distillation with crystallization (Luque et al., 2009), and electodialysis (Kurzrock and Weuster-Botz, 2010). Recently, one-step succinic acid recovery method by direct crystallization was proposed by (Li et al. 2010).

3.1.3. 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, making 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.

3.1.3.1. 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 offers higher efficiency and economic benefits have been developed to overcome and replace the conventional recovery boilers more to offer in terms of efficiency and economic benefits (Larson et al., 2006).

3.1.3.2. 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) and Larson et al. (2006). 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.

3.1.3.3. Black liquor gasification with DME production (BLG/DME). Not only BLG can offer more efficient power supply, but it also 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 et al., 2014).

3.1.3.4. 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 (García et al., 2009; Wang and Chen, 2013; Santos et al., 2014; Lourençon 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 (Sharma et al., 2015).

3.2. 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 1. 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 Fig. 5 along with intervals for the biochemical production in Fig. 6.

3.2.1. 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 re-

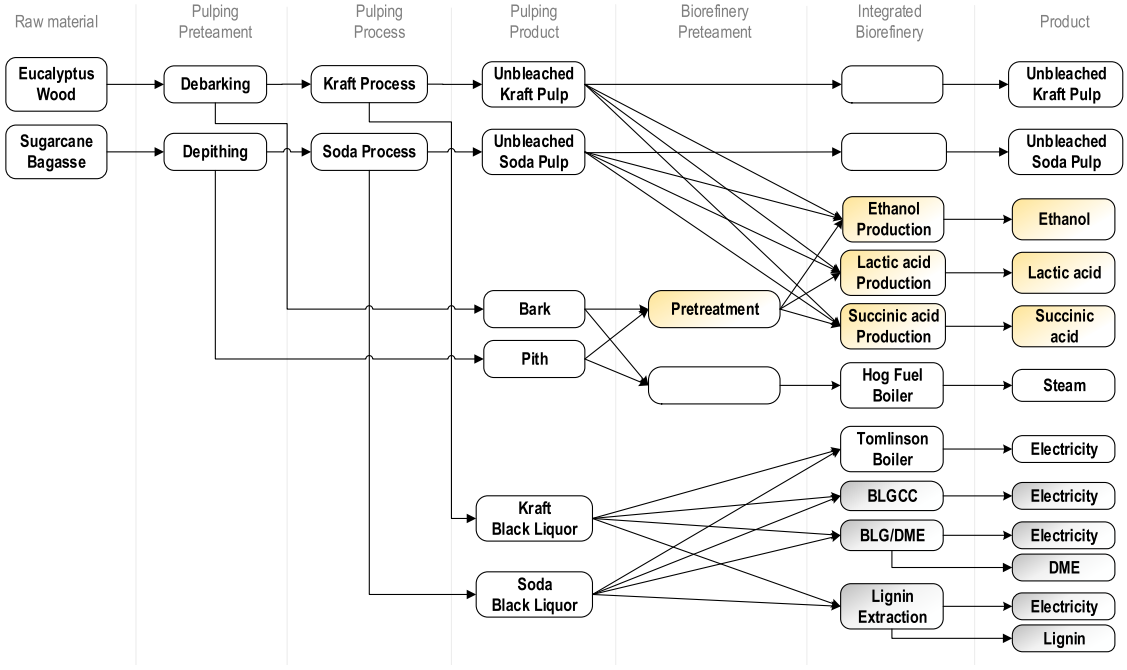

Fig. 5. Overview of superstructure for integrated biorefinery network.

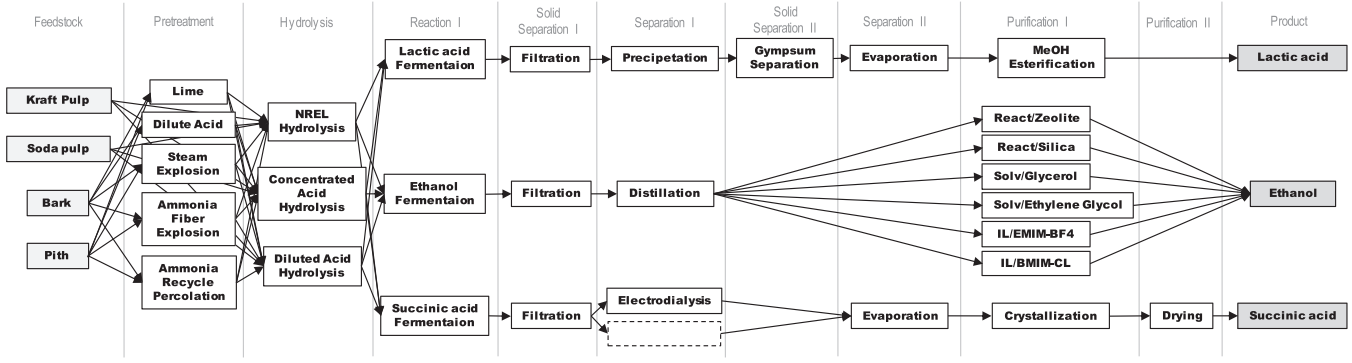

Fig. 6. Superstructure of biochemical production.

Table 1
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

ceptor 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.

3.2.2. Pulping process

3.2.2.1. 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

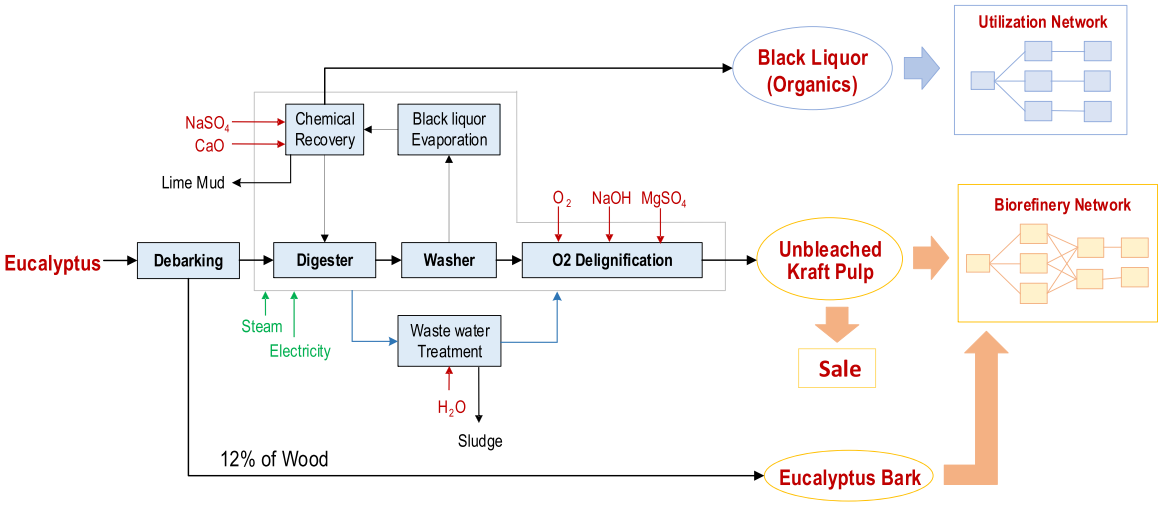

Fig. 7. Kraft process configuration.

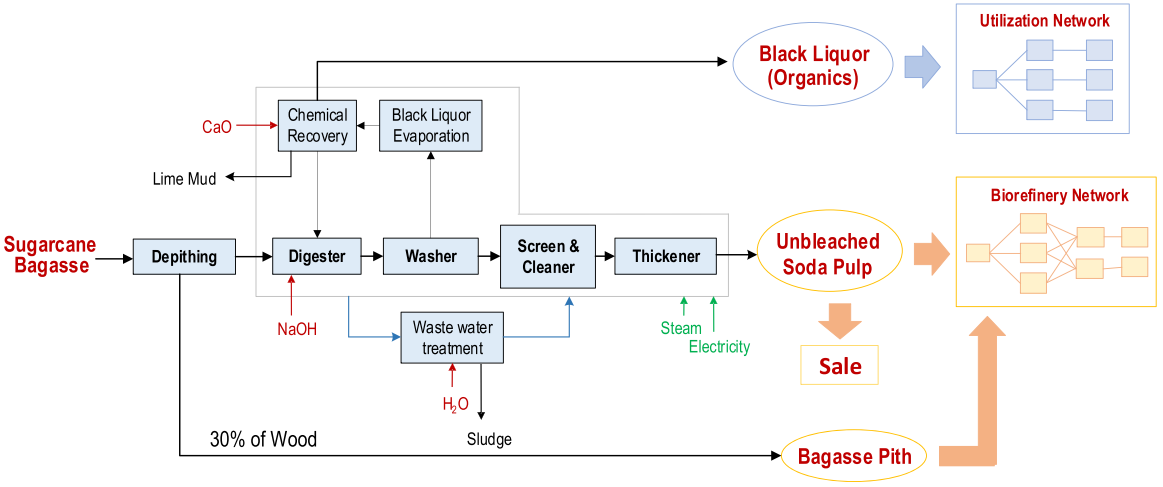

Fig. 8. Soda process configuration.

Kraft cooking process is 45% based on debarked eucalyptus wood chip. The flow-diagram of the Kraft process is displayed in Fig. 7.

3.2.2.2. 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 Fig. 8.

3.2.3. 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.

3.2.3.1. 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 Fig. 6.

3.2.3.2. 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.

3.2.3.3. Succinic acid. For succinic acid production in the generated superstructure (see Fig. 6), 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 electodialysis, the electodialysis step takes place before evaporation and crystallization. An electodialysis separator is applied for base (NaOH) recycle and simultaneously converting succinate to succinic acid.

3.2.4. 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.

3.2.4.1. 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.

3.2.4.2. Black liquor gasification combined cycle. In this paper, high-temperature BLGCC, designed around a technology being developed by Chemrec Company (Sweden) (Chemrec, 2006) 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.

3.2.4.3. 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. (2006). 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 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

Table 2
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. (2006)

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.

3.2.4.4. Lignin extraction. In the superstructure (see Fig. 5), 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).

3.3. 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 2.

3.3.1. 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 produciton 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 3. 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. 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, 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

Table 3
Economic results of an optimal network and compared networks for scenario I.

Network	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 4
Economic results of integrated networks with Kraft process for scenario I.

Network	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

Table 5
Economic results of the optimal networks for scenario II.

Optimization Case	Product Flow (tons/year)	Profit ($/y)	Product Sale ($/y)	Raw material Cost ($/y)	Chemical Cost ($/y)	Utility Cost ($/y)	Capital Cost ($/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)	59,777,186	85,395,389	2,300,000	2,304,623	19,325,516	1,688,064
50% of pulp for paper production: Soda process with succinic acid production and BLG/DME	17,820 (Pulp) 20,022 (SA) 3,950 (DME)	47,261,367	68,097,892	2,300,000	2,037,950	14,811,738	1,686,837
80% of pulp for paper production: Soda process with succinic acid production and BLG/DME	28,512 (Pulp) 12,824 (SA) 3,950 (DME)	34,468,792	49,711,689	2,300,000	1,713,576	9,544,653	1,684,668
100% of pulp for paper production: Soda process with lactic acid production and BLG/DME	35,640 (Pulp) 10,388 (LA) 3,950 (DME)	25,142,769	37,271,188	2,300,000	2,684,113	5,456,404	1,687,902

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 4 shows the results of the integrated networks with the Kraft process.

3.3.2. 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 5. 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 6. 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 in spite of co-production withpaper production.

3.3.3. 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 7 shows product

Table 6
Economic results of the optimal networks with Kraft process for scenario II.

Optimization Case	Product flow (tons/year)	Profit ($/y)	Product Sale ($/y)	Raw material Cost ($/y)	Chemical Cost ($/y)	Utility Cost ($/y)	Capital Cost ($/y)
20% of pulp for paper production: Kraft process with succinic acid production and lignin extraction	7,902 (Pulp) 23,678 (SA)	55,629,750	78,045,576	2,900,000	1,643,336	17,777,943	94,547
50% of pulp for paper production: Kraft process with succinic acid production and lignin extraction	19,755 (Pulp) 15,686 (SA)	43,661,088	60,518,547	2,900,000	1,364,134	12,500,329	92,996
80% of pulp for paper production: Kraft process with succinic acid production and lignin extraction	31,608 (Pulp) 7,694 (SA)	31,693,041	42,992,473	2,900,000	1,084,933	7,223,054	91,445
100% of pulp for paper production: Kraft process with succinic acid production and lignin extraction	39,510 (Pulp) 2,366 (SA)	23,713,317	31,306,831	2,900,000	898,798	3,704,305	90,411

Table 7
Economic results of the integrated biochemical networks with Soda process for scenario III.

Optimization Case	Product flow (tons/year)	Profit ($/y)	Product Sale ($/y)	Raw material Cost ($/y)	Chemical Cost ($/y)	Utility Cost ($/y)	Capital Cost ($/y)
Multiple Biochemical Production							
30% sugar to succinic acid	9,368 (SA) 25,195 (LA) 3,950 (DME)	61,852,523	88,739,715	2,300,000	5,736,474	17,154,697	1,696,021
50% sugar to succinic acid	15,613 (SA) 17,997 (LA) 3,950 (DME)	63,280,904	90,918,941	2,300,000	5,044,575	18,599,480	1,693,982
80% sugar to succinic acid	24,982 (SA) 7,199 (LA) 3,950 (DME)	65,423,616	94,187,802	2,300,000	4,006,616	20,766,647	1,690,923
Multiple Biochemical Production with Pulp Sale							
20% Pulp for paper production	7,128 (Pulp) 10,144 (SA) 19,141 (LA) 3,950 (DME)	55,045,843	79,281,873	2,300,000	4,837,413	15,413,705	1,684,912
50% Pulp for paper production	17,820 (Pulp) 10,140 (SA) 11,363 (LA) 3,950 (DME)	44,487,156	64,614,312	2,300,000	3,621,517	12,521,497	1,684,142
80% Pulp for paper production	28,512 (Pulp) 10,065 (SA) 3,142 (LA) 3,950 (DME)	33,456,826	48,660,739	2,300,000	2,328,670	8,892,119	1,683,124

Table 8
Economic results of the integrated biochemical networks with Kraft process for scenario III.

Optimization Case	Product flow (tons/year)	Profit ($/y)	Product Sale ($/y)	Raw material Cost ($/y)	Chemical Cost ($/y)	Utility Cost ($/y)	Capital Cost ($/y)
Multiple Biochemical production							
30% sugar to succinic acid	8,659 (SA) 21,687 (LA)	54,487,538	78,572,119	2,900,000	5,150,032	15,932,675	101,874
50% sugar to succinic acid	14,432 (SA) 15,491 (LA)	56,749,533	81,638,273	2,900,000	4,450,340	17,438,323	100,077
80% sugar to succinic acid	23,090 (SA) 6,196 (LA)	60,142,527	86,237,503	2,900,000	3,400,800	19,696,796	97,380
Multiple Biochemical production with pulp sale							
20% Pulp for paper production	7,902 (Pulp) 10,130 (SA) 14,430 (LA)	49,418,152	70,591,488	2,900,000	3,978,732	14,202,710	91,895
50% Pulp for paper production	19,755 (Pulp) 10,919 (SA) 5,044 (LA)	38,130,000	57,821,419	2,900,000	2,396,130	11,230,345	90,930

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 also DME productions. As the results in Table 8, 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.

It should be noted that the pulp and paper industry suffers from low profit margins and as such is quite conservative/risk averse when it comes to adopting new technology. To mitigate the risks, the investment of integrated biorefinery facilities should be performed phase by phase to spread the investment cost. To enhance profit of the pulp mill, integrated biochemical production should be the first developed phase for co-production with paper production based on market demand of bioproducts. To replace the expired Tomlinson boiler, black liquor gasification combined cycle with biomass gasification would be developed to supply more energy for integrated biorefinery network. Implemented DME production with gasification process would be performed with potential market demand.

4. Conclusions

Superstructure optimization has been performed to generate optimal integrated network alternatives considering three scenarios that indicate promising 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 also 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 interface 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.

Acknowledgement

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 PhD Program from the Thailand Research Fund and Chulalongkorn University.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.compchemeng.2018.07.019.

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