Superstructure development of lignocellulosic biomass from empty fruit bunch of palm for optimal design of bio-based chemical productions

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การพัฒนาโครงสร้างมหภาคของชีวมวลลิกโนเซลลูโลซิกจากทะลายปาล์มสำหรับการออกแบบที่เหมาะสมของการผลิตสารเคมีชีวภาพ

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นุสรา ปลอดโปร่ง : การพัฒนาโครงสร้างมหภาคของชีวมวลลิกโนเซลลูโลซิกจากทะลายปาล์มสำหรับการออกแบบที่เหมาะสมของการผลิตสารเคมีชีวภาพ. (Superstructure development of lignocellulosic biomass from empty fruit bunch of palm for optimal design of bio-based chemical productions) อ.ที่ปรึกษาหลัก : อ. ดร.พงศ์ธร เจริญศุภนิมิตร

ส่วนประกอบจากต้นปาล์มน้ำมันยกตัวอย่างเช่น ใบ ลำต้น และทะลายปาล์มเปล่า เป็นส่วนที่มีมูลค่าต่ำ ส่วนมากนิยมใช้ในการผลิตปุ๋ย ในความเป็นจริงแล้วหากพิจารณาถึงองค์ประกอบภายในคือเซลลูโลส เฮมิเซลลูโลส และลิกนิน ล้วนเป็นส่วนประกอบที่สามารถนำมาเป็นสารตั้งต้นสำหรับผลิตสารเคมีอื่นๆ ได้ อาทิ ไบโอเอทานอล กรดแลคติก กรดซัลซินิก และสารประกอบอะโรมาติก ในงานวิจัยเรื่องนี้จึงทำการเก็บรวบรวมผลการทดลองเพื่อสร้างเป็นโครงสร้างมหภาคของการแปรสภาพของเสียที่มาจากต้นปาล์มเพื่อเพิ่มมูลค่าเป็นผลิตภัณฑ์ใหม่ได้ สิ่งที่มีความสำคัญสำหรับการพัฒนาสร้างโครงสร้างมหภาคนี้ คือ 1) การเลือกใช้สารเคมี 2) ขั้นตอนและกระบวนการผลิต ซึ่งจะส่งผลต่อความซับซ้อนของทางเลือกในการผลิตที่เป็นไปได้ทั้งหมด อย่างไรก็ตามการหาทางเลือกที่เหมาะสมจะมีผลสอดคล้องกับวัตถุประสงค์ของงานวิจัยเล่มนี้ โดยการแก้ปัญหาความซับซ้อนของโครงสร้างมหภาคจะใช้โปรแกรมแกม (GAMS) ในการวิเคราะห์แบบจำลองเชิงเส้นตรงผสมจำนวนเต็ม (mixed integer nonlinear programming, MINLP) เพื่อหาเส้นทางที่เหมาะสมตามวัตถุประสงค์ของงานวิจัย ผลการวิจัยพบว่า กรดซัลซินิก สามารถให้ผลกำไรมากที่สุดประมาณร้อยละ 89 เมื่อเทียบกับราคาต้นทุน ตามด้วย กรดแลคติก และไบโอเอทานอล นอกจากนี้เมื่อวิเคราะห์ความแปรผันของราคาผลิตภัณฑ์ จะพบว่าเส้นทางที่ดีที่สุดของทั้งสามผลิตภัณฑ์ มีความแตกต่างกัน สุดท้ายเมื่อทำการพิจารณาระหว่างการผลิตสารเคมีคือ กรดแลคติกและกรดซัลซินิก พบว่าวิธีเดียวที่สามารถทำให้ทางเลือกที่ดีที่สุดผลิตกรดแลคติกแทนกรดซัลซินิก คือราคาขายของกรดแลคติกต้องมากกว่ากรดซัลซินิก ผลการทำวิจัยในการเลือกเส้นทางของโครงสร้างมหภาคนี้จะเป็นการเสนอทางเลือกที่มีศักยภาพเพื่อใช้ในการออกแบบกระบวนการต่อไปภายภาคหน้า

สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต ....
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KEYWORD: CELLULOSE HEMICELLULOSE LIGNIN SUPERSTRUCTURE MIXED INTEGER NONLINEAR PROGRAMMING(MINLP)

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Apart from palm oil, the left-over parts of palm trees such as leaves, trunks and empty fruit brunches are low in value that typically used for producing fertilizer. In fact, considering the constituents in these wastes, they comprise of valuable components including cellulose, hemicelluloses and lignin. Recovery of these components is beneficial since they can be used as precursors for a wide range of productions of other chemicals such as bio-ethanol, succinic acid, lactic acid and other aromatic compounds. In this work, therefore, we gather experimental works in the literature in order to establish a super-structure, the network of processes that links the waste obtained from palm trees to the higher-value products. This super structure development is of importance for 1) the selection of produced chemicals and 2) the optimal process design since it provides the whole possible products and production alternatives. However, the constructed structure can be complicated specifically the selection of the best pathway which depends on the objective functions. To remedy this, we utilize mixed integer nonlinear programming (MINLP) in GAMS to search for the best pathway subject to the specified objective functions. According to the obtained results succinic acid provides the highest profit margin - about 89 %profit relative to the investment cost followed by lactic acid and ethanol. In addition, the optimal pathways of synthesis specific to each product, e.g. lactic acid, succinic acid and bioethanol are determined given variability of the

Field of Study: Chemical Engineering Student's Signature ....

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Introduction

1.1 Background

Oil palm is one of the major economic crops in Thailand especially in the food and energy sectors. In Thailand, there are more than 200,000 palm cultivators and more than 1,800 merchants who own pieces of land for palm plantation, collect and sell oil for the palm oil refinery (Agricultural Research Development Agency (Public Organization), 2015). Such high numbers of cultivators and merchants are resulted from the fact that the products from palm (e.g., oil) are more profitable than other crops such as rubber and rice. This; therefore, motivates the farmers to start the plantation of palm or expand their existing palm plantation capacities (Mueangdee, 2012). Thanks to such growing popularity of the plantation of palm, Thailand has become the third largest producer of palm worldwide ranked after Indonesia and Malaysia.

Although the farmers and the palm-land owners have gained immense advantages from the expansions of the plantation of palm, such expansions inevitably result in the growing amounts of solid waste known as the palm biomass such as empty fruit bunch, palm kernel shell, mesocarp fiber, palm frond, and palm trunk. Factually, the most profitable product from palm, the extracted oil, contributes only about 10% of the total useful parts of the whole palm tree - the remaining 90% are the palm biomass (Loh & Choo, 2013). There are a number of ways for disposal of the biomass including 1) a combustion of the biomass for electricity generation (Lertsiri, 2008), 2) a utilization of the biomass as mulching material that eventually decomposes to biological fertilizer (Sukiran et al., 2017) and 3) a use of the biomass as additives in livestock food (Sukiran et al., 2017).

As seen from the utilizations of the biomass mentioned previously, the value of the biomass from palm is relatively low. This has led to a need of any methodologies that can provoke the full utilization potentials of the biomass. According to the literature, there have been many attempts to harness the full potentials of the biomass specifically the conversion of the biomass into bio fuel or other value-added products

(Agricultural Research Development Agency (Public Organization), 2015). Thanks to its useful constituents, the conversion of the biomass to more valuable products has gained continual attentions recently since the biomass contains a structure of lignocellulosic network.

Interests in the utilization of the lignocellulosic biomass for the production of value-added products have increase significantly in the recent years because of its beneficial ingredients including cellulose, hemicellulose and lignin (H. Zabed et al., 2016). Among the biomass of palm mentioned previously, the empty fruit bunches (EFB) are the most interesting part of palm due to their abundance that are readily available as residuals from the harvests of palm fruits (Economics, 2013).

Typically, the empty fruit bunches are burnt to generate heat for the electricity generation in palm mills. However, burning the biomass can have the adverse effects on the environments since it releases an excessive emission of white-ash smog to the atmosphere. Such high ash content smog may be associated with the increasing emissions of NO_x (Loh, 2017) as well as the PM 2.5 levels that should be avoided. In fact, the more environmentally friendly use of the empty fruit bunches is currently used via mulching material and fertilizer. However, doing such are not recommended as the beneficial contents of lignocellulosic biomass are not fully utilized. To recommend the better use of this lignocellulosic biomass, the whole picture of possible processing routes of the empty fruit bunches for the production of higher value chemicals are required.

Thus, this thesis focuses on 1) gathering the experimental information regarding the processing steps of the lignocellulosic biomass, 2) establishing a large network of processing pathways known as the superstructure that connects the upstream (e.g. the empty fruit bunches) to the downstream (i.e. the value-added chemicals such as ethanol) and 3) identifying the most suitable processing route with the assistance of mathematical optimization techniques which is subject to the user-defined objective functions (e.g. maximized profit, minimized amount of utility and etc.). Accordingly, this superstructure development is of importance for 1) the wholly picture of the processing routes associated with the palm biomass which allows visualization and alternative-search of all production possibilities, 2) the selection of the potential chemicals that are likely to return profit, and 3) the identification of the most optimal processing pathways specific to the selected chemicals. The acknowledgement of the importance of the superstructure has led to the objectives and scopes of this work provided in Sections 1.2 and 1.3 respectively.

1.2 Objective

The objectives of this work are divided into two sections as follows

1.2.1 Objectives in superstructure development

- To gather information regarding the pretreatment processes of the empty fruit bunch in producing the cellulose, hemicellulose and lignin.
- To identify the task of each pretreatment process and its significance in the developed superstructure.
- To study processes of transformation of the products obtained after the pretreatment processes into the selected chemicals such as ethanol.
- To describe the input-output structure contained in the developed superstructure in terms of the mass balance and the required amounts of utility associated with each processing block.

1.2.2 Objectives in determination of optimal pathway

- To specify a suitable optimization algorithm for the developed superstructure.
- To identify the most optimal processing pathway using the selected optimization algorithm that is subject to the objective functions.
- To determine the most feasible route of the empty fruit bunch processing in order to produce the selected chemicals (e.g. lactic acid, succinic acid and bioethanol).

1.3 Scope of research

As mentioned previously, the empty fruit bunch is selected for the processing biomass because this part of palm is abundant and is readily available after completion of the palm fruit harvest. Details about the scope of this work are provided below;

- Maximization of profit (Scenario I)
- Optimal processing route specific for each chemical (Scenario II)
- Sensitivity of the product prices to the most profitable chemical and optimal processing pathway (Scenario III)

1.4 Schedule plan

No.	Activity	Monthly Program (2018-2019)						
		Aug	Sep	Oct - Dec	Jan - Mar	Apr - Jun	Jul - Sep	Oct - Dec
1	Review and overview - Processes and products of oil palm in Thailand - Current utilization of oil palm biomass in Thailand - Pretreatment processes of palm biomass to sugar monomers - Approaches of lignocellulosic conversion of palm biomass to ethanol.	■	■	■	■	■		
2	Mass balance calculations Determine the mass balance in each unit block and collect data of ash-free and dry basis of biomass			■	■	■	■	■

3	Superstructure generation Create a superstructure				■	■	■	■
4	Superstructure optimization - Convert the superstructure into mathematical model for optimization - Determine the best route of processing subject to the specified objective function							■

Chapter 2

Theory and literature reviews

2.1 General information of oil palm

Oil-palm is a useful plant that its components can be used as food and energy sources. Such indispensable sources we consume everyday are partly derived from palm tree such as oil from palm fruit and the left-over biomass such as palm kernel shell, mesocarp fiber, and etc. (Lertsiri, 2008). Among these, palm oil is the most required component from palm due to its application in food, pharmaceutical and energy industries.

As depicted in Figure 2.1, oil palm has the highest production capacity when compared to other oil crops – about 6 to 10 times larger than other oil crops per rai (Petchseechoung, 2017). Although the plantation of palm is smallest compared to other oil crops, the production amount of oil palm turns out to be highest which results in the cheapest production cost per kilogram of palm fruits. Accordingly, many agricultural-based countries have begun to grow oil-palm and turn it into their national economic crop. There are three major ways to make use of palm including food: processed palm oil for the direct consumption, oleochemicals: transformation of palm oil into commodity products such as soaps and energy: biodiesel (Channiyom, 2016).

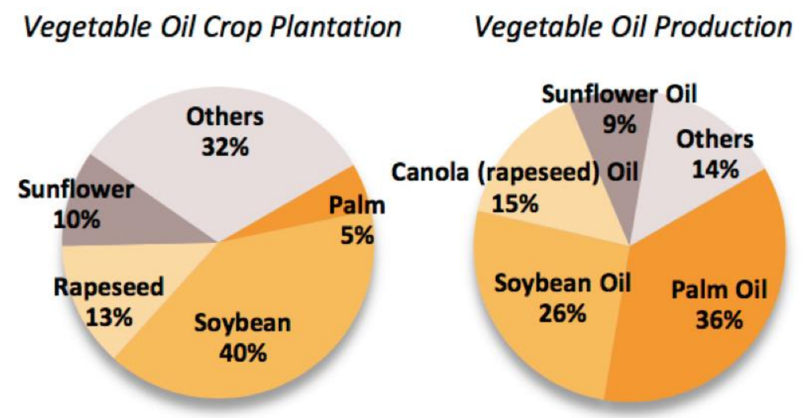


Figure 2.1: Distributions of World Vegetable Oil Plantation and Production (Petchseechoung, 2017)

2.2 Components in oil palm

There are five major components in oil palm including, trunk, frond, fruit, Empty fruit bunch, kernel shell and Mesocarp fiber.

2.2.1 Oil palm trunk

Typically, the life-cycle of palm tree is approximately 25 years. After that the tree is cut due to the decrease of palm fruit yield or the too-high tree that leads to difficulty in fruit collections. After the tree is cut, burning or using it as mulching material are common practices to make use of this almost useless biomass (Selamat et al., 2014).

2.2.2 Oil palm frond

Leaves of palm tree or fronds are available throughout the year as they are regularly cut during pruning and harvesting of fresh fruit bunch (Ooi et al., 2017). Leaves are divided into 2 parts: leaflets and petiole. Usually, cultivators harvest palm fruits every 15 days. Approximately, 44 petioles are cut per 4 Rai (Chanjula, 2015).

2.2.3 Oil palm fruit

Oil-palm fruit has no sessile drup. The shapes of fruits vary from being oval to being elongated with 2 - 5 centimeter long and 3 - 30 grams per fruit. The ripe fruits have red or orange colors which oil can be extracted in this layer. Fruit collections start at about 30 months from the date of planting and the collections continue throughout the year. It is approximated that palms yield about 3,000 kilograms oil per rai per year. The harvest cycle is within the range of 10 - 20 days depending on the season. The average harvest rate is about every 15 days (Channiyom, 2016).

2.2.4 Empty fruit bunch

Empty fruit bunch is a biomass residual abundantly available after the separation of palm fruits. It contains neither chemical nor mineral additives and free from foreign elements such as gravel, nails, wood residues, and waste (Ooi et al., 2017). A palm bunch consisting of stalks (45 - 70 % of the total mass) and palm fruits. The bunch that carries ripe fruits weighs about 1 - 60 kilograms. The collections of palm bunches coincide with the collections of the palm fruit as they are collected simultaneously and are separated in a rotating drum in the palm oil refining plant. (Economics, 2013).

2.2.5 Palm kernel shell

Palm kernel shell is residue obtained from the removal of palm kernel during the oil extraction process. The shell layer that covers the nut is removed after crushing in the palm oil mill. The shell is fibrous material and can be easily handled in bulk. (Ooi et al., 2017).

2.2.6 Mesocarp fiber

Mesocarp fiber is a residue obtained from the oil extraction of mesocarp. This natural fiber is extracted as a by-product from sterilization and milling processes of fresh fruit bunch (Ooi et al., 2017).

2.3 Current sources and destinations of palm components

As seen from the components of palm in Section 2.2, these components can be grouped into two categories. The first category is palm fruit which is mainly considered as the profitable component that gives palm oil. This component is typically delivered to palm mills in order to extract crude palm oil for edible products and biodiesel production (industry, 2009). The second category is the fiber-based biomass which includes palm trunk, palm frond, empty fruit bunch, palm kernels and mesocarp fiber.

With regard to the fiber-based biomass of palm, Sukiran et al. (2017) conducted studies regarding the current utilizations of this type of biomass. According to his work, the fiber-based biomass is available from two different sources. Trunks and pruned fronds are the first form of biomass available from plantation land sites. Palm fronds are available continuously as a result of a pruning process during the fruit harvest whereas palm trunks are available during the replanting process. Empty fruit bunch, mesocarp fiber and palm kernel are the second form of biomass available from oil extraction mills. The empty fruit bunch is collected after the fruits are stripped from the bunch via the high-pressure cooking process. The mesocarp fiber is produced during the oil extraction process while the kernel shell is obtained after the process of separation of nut from its kernel (Petchseechoung, 2017).

Figure 2.2 illustrates the current utilization of fiber-based biomass. Normally, this type of biomass is used as mulching material, used as additives in livestock food or disposed of in flare. For example, palm mills have combustion chambers where the mesocarp fiber and palm kernels are burnt in order to boil water for steam generation which eventually produces electricity (Sukiran et al., 2017). In addition to the direct combustion, the fibrous material can be used as reinforcement in wood composites. For example, Then et al. (2013) studied the use of mesocarp fiber as a filler in fiber-reinforced composites which proved that this utilization approach was technically feasible. Chanjula (2015) studied the potential use of palm frond as a fiber source for ruminants. He also showed that the palm frond can be converted into pulp. Wanrosli et al. (2007) showed that frond pulp may be used as a reinforcement component in a newsprint production using softwood thermomechanical fibers.

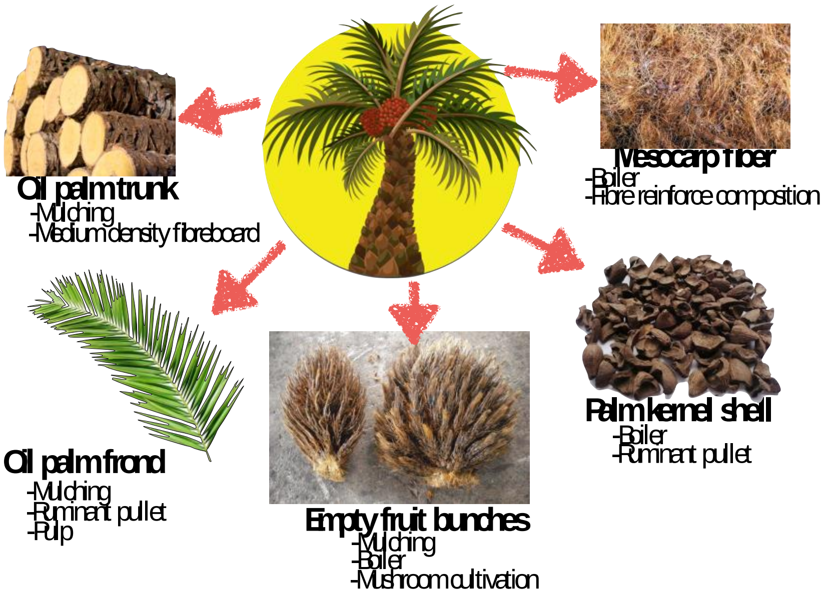


Figure 2.2: Current utilization of fiber-based biomass from palm (Sukiran et al., 2017)

Further, palm trunk can be used for a manufacturing plywood (Hoong et al., 2013). Lastly, empty fruit bunch is the most abundant biomass that is readily available from the palm oil industry throughout the year. Because of its enriched organic matters and nutrient contents, empty fruit bunch is directly used as mulching material in palm plantation. In fact, all this fiber-based biomass has not been used to its full potentials as seen from the current utilizations. By considering the constituent contained in this type of biomass, it can be value-added since the fibrous material contains a lignocellulosic network which is made of cellulose, hemicellulose and lignin.

2.4 Lignocellulosic materials in fiber-base biomass of palm

Lignocellulosic network in palm biomass contains a mixture of cellulose, hemicelluloses, and lignin as depicted in Figure 2.3. Typically, a distribution of constituents in the lignocellulosic network depends on the types of biomass from palm (Sukiran et al., 2017) as listed in table 1.

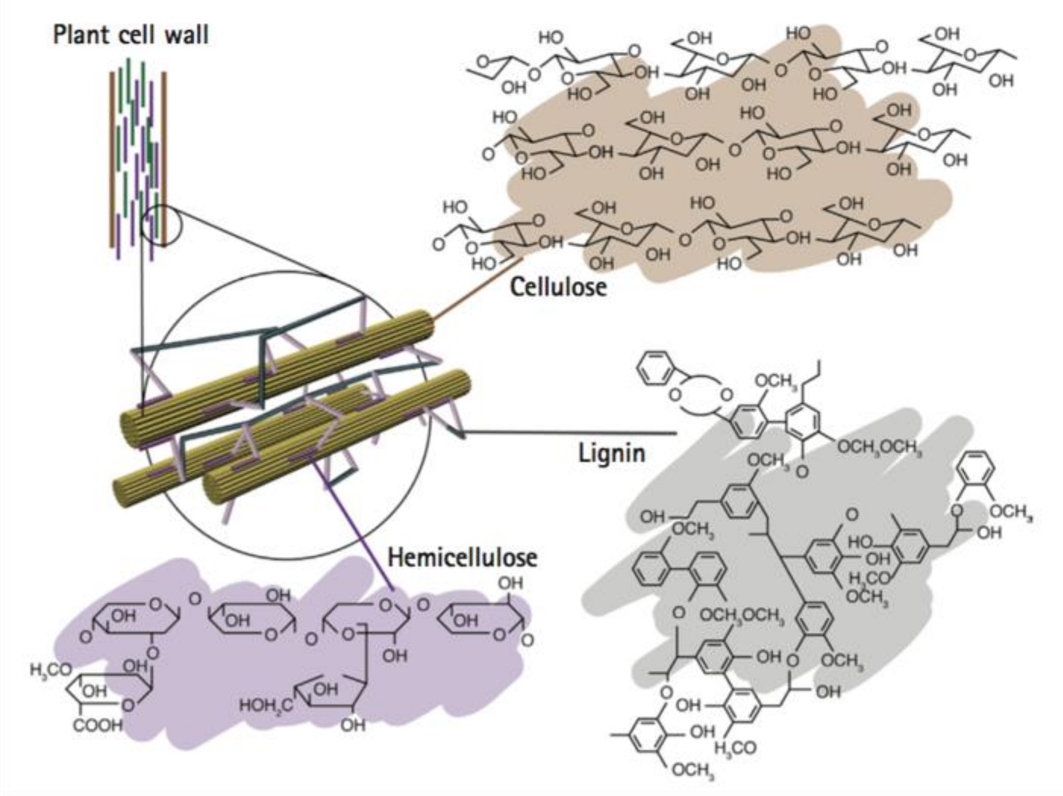


Figure 2.3: Plant cell wall and lignocellulosic biomass composition

(Jaya Shankar Tumuluru et al., 2011)

Table 2.1: Chemical compositions of biomass from palm

(Kong et al., 2014)

Site	**Type of oil palm solid waste**	**Chemical components (%dry wt.)**				
		Cellulose	**Hemicellulose**	**Lignin**	**Extractive**	**Ash**
Oil palm mill	Empty fruit bunches	38.3	35.3	22.1	2.7	1.6
	Palm kernel shell	20.8	22.7	50.7	4.8	1.0
	Mesocarp fiber	33.9	26.1	27.7	6.9	3.5
Plantation	Oil palm trunk	34.5	31.8	25.7	3.7	4.3
	Oil palm frond	30.4	40.4	21.7	1.7	5.8

The information given in the table 2.1 displays the main components of lignocellulosic network including cellulose, hemicellulose and lignin. In the molecular level, cellulose and hemicellulose polymers are firmly linked to lignin through covalent and hydrogen bonds making the structure highly robust and recalcitrant to depolymerization (Limayem & Ricke, 2012).

2.4.1 Cellulose

Cellulose is a linearly-structured component contained in a plant cell wall which consists of a long chain of glucose monomers linked thorough the β(1->4)-glycosidic bonds. The bonds can reach several thousand glucose units in length as shown in Figure 2.4. The extensive hydrogen linkages among molecules contribute to a crystalline and strong matrix structure of cellulose (Limayem & Ricke, 2012).

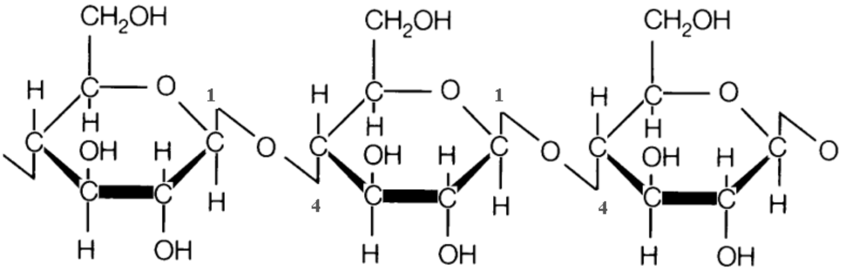
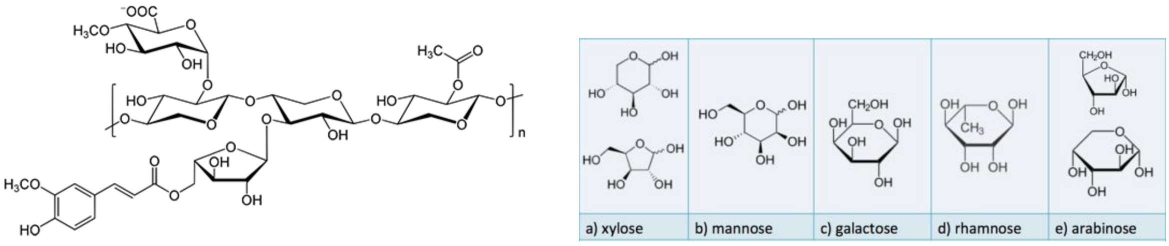


Figure 2.4: β(1->4)-glycosidic bonds of glucose contained in cellulose (Pornchaloem & Rattanapanon, 2010)

2.4.2 Hemicellulose

Hemicellulose is an amorphous form of heteropolymers including hexose (D-glucose, D-galactose and D-mannose) as well as pentose (D-xylose and L-arabinose). Hemicellulose may contain sugar acids (uronic acids) such as D-glucuronic, D-galacturonic and methylgalacturonic acids. The spine chain of hemicelluose consists primarily of xylan (β(1->4)-linkages) that includes approximately 90% of D-xylose and 10% of L-arabinose (Girio et al., 2010). Xylan appears predominantly in hemicellulose but the chemical compositions of xylan vary depending on the sources of biomass. (F. Yusuf & N.A. Gaur, 2017). Because of the diversity of sugars, xylan, a representative component of hemicellulose requires a wide range of enzymes to be completely hydrolyzed into free monomers (Limayem & Ricke, 2012). As shown in Figure 2.5, hemicellulose consists of many types of sugar molecules connected together such as xylose, mannose, galactose, rhamnose and arabinose



(a) (b)

Figure 2.5: Chemical structure of hemicellulose (a) and sugar monomers contained in hemicellulose (b)

(John, 2017)

2.4.3 Lignin

Lignin is an amorphous, highly branched, cross-linked macromolecular polyphenolic resin with no exact structure. Lignin occupies spaces in the cell wall between cellulose, hemicellulose, and pectin. Lignin is covalently linked to hemicellulose and cross-links to plant polysaccharides. These links are contributed to the mechanical strength of the cell wall, Lignin is relatively hydrophobic and aromatic in nature. The degree of polymerization of natural lignin is difficult to measure since lignin is fragmented during extraction and the molecule consists of various types of substructures that appear to repeat in a haphazard manner (Jaya Shankar Tumuluru et al., 2011).

As seen from the chemical compositions found in lignocellulosic material, it is very complicated which leads to non-simple method of pretreatments. The suitable method and conditions of pretreatment depend greatly on the type of lignocelluloses. Currently, palm biomass is converted into various value-added products via different available conversion technologies or conventional practices. Details about the pretreatments are given in the next section.

2.5 Pretreatment of biomass

Pretreatment in general is a process that causes dissociation of the lignocellulosic network. As shown in Figure 2.6, pretreatment of lignocellulosic biomass aims to decrease the crystallinity of cellulose, increase the biomass surface area, remove hemicellulose content, and break the lignin seal (Pawongrat, 2015). The dissociation of the lignocellulosic network enhances the enzymatic activity since the hydrolysable ingredients such as cellulose and hemicellulose are more accessible to the enzyme. This leads to a higher rate of enzymatic reaction of carbohydrate polymers into fermentable sugars (Jin-Suk Lee et al., 2008), which eventually contributes to higher yield of the desirable products.

Pretreatment can be divided into 4 main methods including physical, chemical, physicochemical and biological pretreatments. Since the pretreatment process is one of the expensive processing steps for production of sugar from biomass, types of the pretreatment merit detailed discussions for an optimal selection of the pretreatment that is suitable for the biomass of interest.

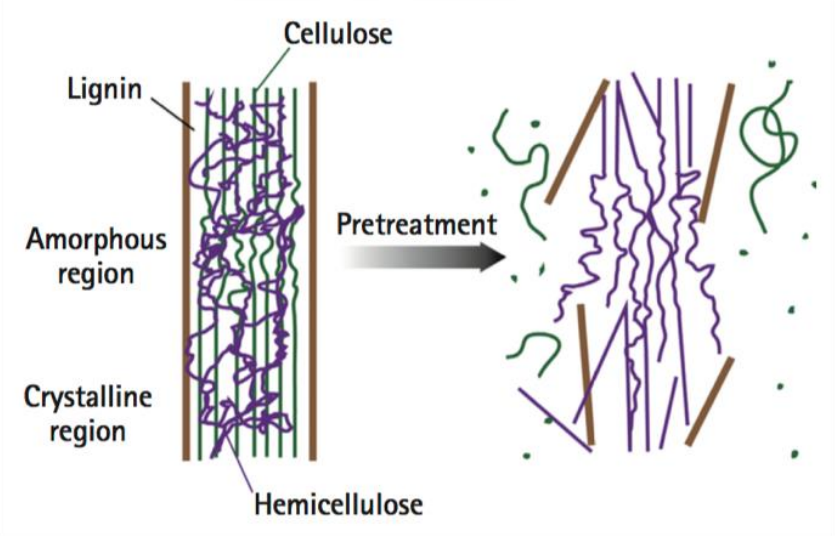


Figure 2.6: Effect of pretreatment on lignocellulosic network contained in agricultural biomass

(Jaya Shankar Tumuluru et al., 2011)

2.5.1 Physical pretreatments

There are 3 main methods for physical pretreatmentห including mechanical comminution, pyrolysis and steam explosion. The mechanical comminution is the processes for reduction of solid materials from a larger average particle size to a smaller one such as crushing, grinding, cutting and vibrating. The comminution normally results in the reduction of cellulose crystallinity and increases the surface area of the biomass (Pawongrat, 2015).

The pyrolysis is a baking process of biomass operating at high temperatures of about 450 °C – 600 °C in a non-oxygen environment. Heat is applied externally causing the breakdown of biomass into gas, liquid, and residuals (Roddy & Manson-Whitton, 2012).

In steam explosion, the steam penetrates the lignocellulosic material to form liquid water inside the fibers at high pressures. After sudden decompression of the pressurized system, liquid water is quickly vaporized which explodes the fibrous structure. The steam explosion destroys the lignocellulosic network which usually operates at moderate temperatures of 150 °C - 180 °C (Pawongrat, 2015).

2.5.2 Chemical pretreatments

There are 3 main methods for chemical pretreatments include ozonolysis, alkaline and chemical pretreatments.

For ozonolysis, ozone acts as an effective oxidant that causes the breakdown of lignin and hemicellulose in the lignocellulosic network. Sun and Cheng (2002) used the ozonolysis as the pretreatment of straw. It was found that the degradation was essentially targeted to lignin with slight degradation of hemicellulose. This method provided some advantages. For example, cellulose was hardly decomposed, toxic was not discharged to the environments and this method can be performed at room temperature. However, a major disadvantage of this method associates with its high cost of operation.

For alkali pretreatment, the alkali typically used for the removal of lignin is sodium hydroxide, potassium hydroxide and ammonium hydroxide. Alkaline hydrolysis involves the saponification of intermolecular ester bonds that connect xylan hemicelluloses and other components altogether. The porosity of the lignocellulosic biomass increases as a result of the removal of the cross-links (Singh et al., 2014). Kim et al. (2008) studied the alkaline pretreatment in barley with ammonia. They found that treatment with ammonia at a concentration of 15 % and temperature of 75 °C for 24 - 72 hours can extract about 50 - 66 % of lignin.

For acid pretreatment, many studies have been conducted using sulfuric acid, hydrochloric acid, phosphoric acid and nitric acid. The acid pretreatment improves digestions of hemicellulose and some portion of amorphous cellulose in the hydrolysis process. Linde et al. (2008) found that the acid pretreatment enhanced the recovery of hemicellulose as monomer dissolved in the liquid fraction and also enhanced the amount of digestible cellulose present in the solid fraction. Though effective as the pretreatment agent, concentrated acids such as sulfuric acid and hydrochloric acid are toxic, corrosive and hazardous by their nature. Therefore, in the process of conditioning of the raw material, utilization of diluted acid is preferred and widely studied (Mussatto et al., 2005). Uric acid or phosphoric acid are often used for the enhanced recovery of hemicellulose, followed by the use of enzymes as catalysts in the hydrolysis reaction for the production of glucose (Silverstein et al., 2007).

2.5.3 Biological pretreatment

This process is another popular method of pretreatment due to that 1) it is eco-friendly (Sindhu et al., 2016), 2) it requires less energy, less inhibitors and 3) it has the potential to produce other products (Chen et al., 2014). Using of microorganisms as pretreatment agent can condition the lignocellulosic content in biomass that increases the digestive efficiency of enzymes without decomposition of cellulose. The work of Hossain exemplifies this biological pretreatment advantage - white-rot fungi was proven great potential for the production of biofuels (Zabed et al., 2019). Ramesh Kuhad et al. (1997) studied the degradation of lignocellulosic network using soft-rot fungi. It appeared that the fungi can extensively degrade cellulose and hemicellulose with slight effect on lignin. In addition, the use of bacteria in pretreatment process is also available in literature. Bacteria slowly digests biomass because it cannot penetrate the lignocellulosic network by itself. However, bacteria usually invade along with fungi which the bacteria may provide essential vitamins or growth promoters to fungi according to Daniel and coworkers (Daniel et al., 1987).

2.5.4 Physicochemical pretreatment

This process is the combination of physical and chemical methods of pretreatments. Wang et al. (2019) studied effect of physicochemical pretreatment and enzymatic hydrolysis on lignocellulosic network. Physicochemical pretreatment removes lignin by attacking the glycosidic linkage in the cell wall matrix in order to degrade the lignocellulosic network and reducing sugar yield. Zhang et al. (2015) studied the method of extrusion combined with alkali pretreatment in the production of methane from rice straw. It was found that the energy efficiency improved from 38.9% (milling only) to 59.9% when extrusion combined with NaOH pretreatment was used.

Table 2.2 provides the summaries of pretreatment methods of lignocellulosic biomass. The purpose of each method of pretreatment as well as the associated advantages and disadvantages are also provided.

Table 2.2: Summaries of pretreatment methods of lignocellulosic biomass (Zabed et al., 2019)

Type of pretreatment	**Major effect on biomass structure**	**Advantage**	**Disadvantage**
Physical	- Increase porosity - Decreased crystallinity of cellulose - Improved accessibility to enzymes	- Easy handling - Improved mass and heat transfer in the subsequent hydrolysis and fermentation - High hydrolysis yield	- High energy input - Original structure of lignin is altered - Not economically feasible

Chemical	- Increase porosity - Removal of hemicellulose - Degrade and slightly alter lignin structure - Enhanced digestibility - Solubilization of hemicellulose	- High reaction rate - Well-studied technique - Excess acid can be recycled - Requirement of low temperature and pressure - Improved hydrolysis - Good for low-lignin biomass	- Low lignin solubilization - Corrosion of process equipment - Requirement of neutralization of pH
Biological	- Delignification of biomass - Structural alteration of cellulose and hemicellulose	- Low cost - Eco-friendly - No release of toxic compounds - No effluent generation - No inhibitor formation	- Long incubation time - Slow rate of delignification - Carbohydrate loss - Risk of health hazard
Physicochemical	- Increased surface area - Effective lignin removal - Increased cellulose digestibility	- High solid load - Low temperature - Low sugar degradation	- Total utilities costs are larger

Pretreatment is an important stage in the transformation of lignocellulose. Without pretreatment, enzymatic hydrolysis cannot be performed at its full potential as seen from low yield and rate of conversion (Guo et al., 2018). The pretreatment process can change the lignocellulose into polysaccharide. However, the polysaccharide must be changed into sugar monomer since the valued-added product such as ethanol is synthesized from the sugar monomer such as glucose. The polysaccharide is changed into sugar monomer by a hydrolysis process which is given in the next section.

2.6 Hydrolysis

The whole process mainly consists of 1) the hydrolysis of polysaccharide into fermentable sugars, 2) fermentation of sugars and 3) separation of the fermented broth. Various methods are available for the production of sugars from lignocellulosic biomass, of which the chemical and enzymatic methods have been proved to be more successful (Sindhu et al., 2016).

2.6.1 Acid hydrolysis

Acid hydrolysis is carried out using acid solution. Although concentrated acid solution of hydrolysis results in high yield of fermentable sugars, the use of acid is toxic, corrosive, and hazardous and require a reactor that can endure the corrosion. This in turn makes the process very expensive. Hence, people are looking for more environment-friendly and economically feasible techniques for deriving sugars from lignocellulosic biomass. Dilute acid hydrolysis followed by enzymatic hydrolysis is one of them. Dilute acid hydrolysis has also been successfully developed for pretreatment, and it significantly improves the efficiency of the enzymatic hydrolysis step. Sulfuric acid concentration below 4% is generally used as it is comparatively inexpensive and helps in achieving high reaction rates. Since sugar decomposition takes place at moderate temperature, this process requires high operating temperature and neutralization of pH before the downstream enzymatic hydrolysis or fermentation processes. Apart from this, to make the process economically feasible, these acids must be recovered from the reaction mixture after hydrolysis (Sindhu et al., 2016).

2.6.2 Enzymatic hydrolysis

Enzymatic hydrolysis is carried out by cellulase enzyme that is highly specific. The products of the hydrolysis are reduced sugars such as glucose. Difference from the chemical hydrolysis is that the enzymatic hydrolysis is conducted at mild conditions - at a pH of 4.8 and temperatures of 45-50 °C, which is optimum for the cellulase enzyme. The main advantage of the enzymatic hydrolysis over than the chemical hydrolysis is that it does not cause corrosion problem (Duff & Murray, 1996). But this process takes several days while the chemical hydrolysis takes only a few minutes. Moreover, the final product of enzymatic hydrolysis inhibits the enzyme and ultimately affects the process unless they are removed immediately after the products occur. Apart from this, a major bottleneck in application of the enzyme in lignocellulose, such as in ethanol production at present, is the cost of the enzymes.

After hydrolysis process, the sugar monomer is fermented to produce value-added products such as ethanol. Detail about the fermentation is given in the next section.

2.7 Fermentation

Fermentation involves a complex system of reactions caused by microorganisms that may be commercially available. The two main types of microorganism used for fermentation are yeast and bacteria. Bacteria is mainly used for gas fuel production such as biogas. As mentioned earlier in Section 1.3, the main type of fermentation is the use of yeast for sugar fermentation to produce ethanol, CO_2 and other aromatic compounds (Fernández & Sánchez-Seiquer, 2003) which is considered in this work.

After studying the alternatives of chemical production processes from empty fruit bunches, the superstructure will be created using the Super O software.

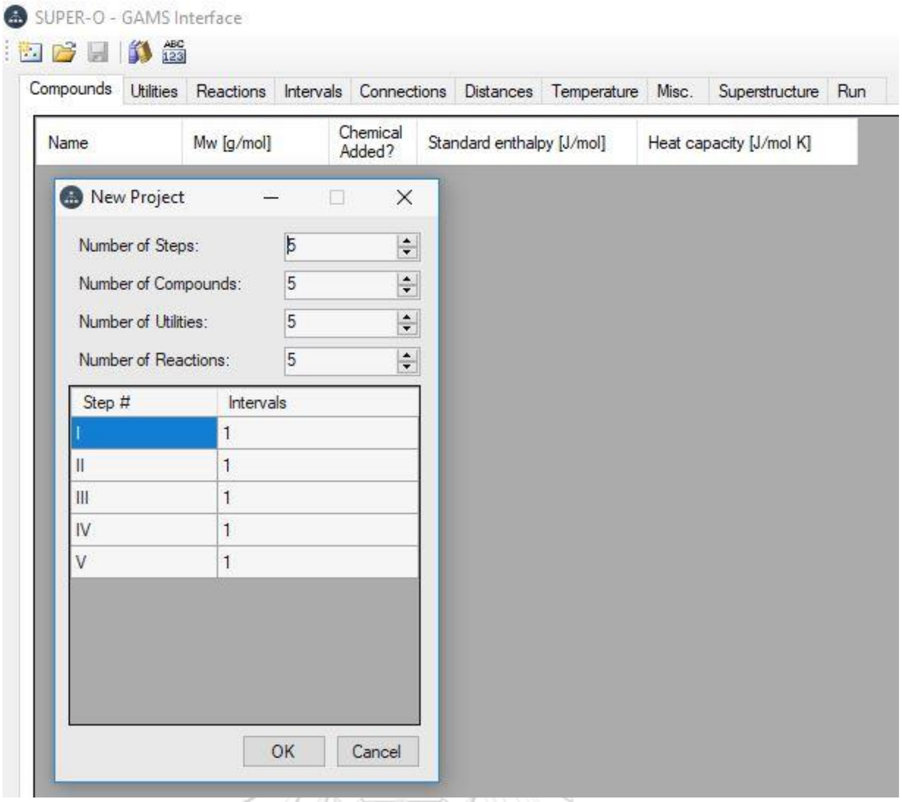
2.8 SUPER-O software

A chemical company is an enterprise which operates the business of transforming raw materials into value-added products, through a series of physical and chemical operations, which constitutes a chemical process. Chemical processes can have different levels of complexity, spanning from simple cases in which the transformation is constituted by a single processing step, to more complex cases, in which several transformation steps are operated in an integrated manner, so that the product of a process step becomes the raw material for the next one. In the latter case, each individual process becomes a node of a complex processing network, through which the transformation of several resources and raw materials into different products is realized (Quaglia et al., 2012). This program connects the alternative pathway of the study above and creates a superstructure based on mass balance data.

The optimal design of a processing network from an enterprise-wide perspective is a complex decision-making problem, which requires the integration of a number of different disciplines and knowledge. Because of the relevance of the problem, in recent years many authors have focused on the development of systematic methods for synthesis and design of processing networks. Through their work, these researchers aimed at developing methods, tools and formal approaches allowing designers to identify better design, while at the same time reducing the time and resources needed for the design problem

2.8.1 Program characteristics

When creating a superstructure, it is necessary to include information such as substrate, chemical added, reaction data, etc. shown in fig.2.7. Which the initial step must start from new project.



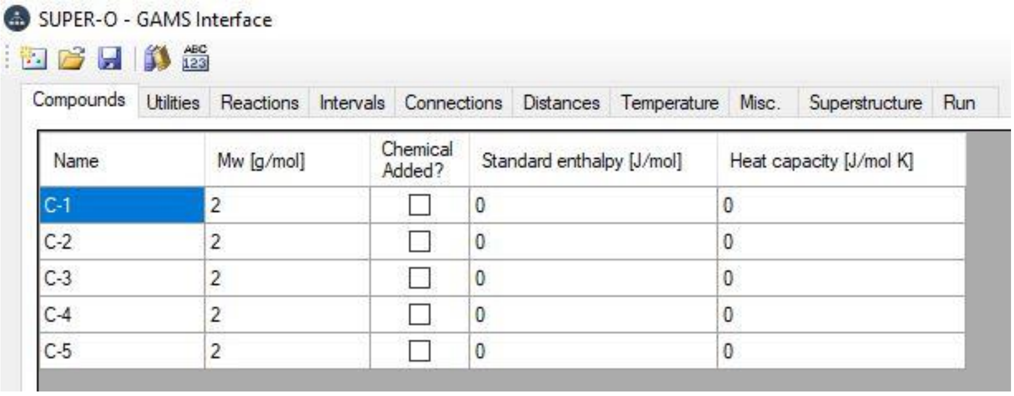
Name	Mw [g/mol]	Chemical Added?	Standard enthalpy [J/mol]	Heat capacity [J/mol K]

Number of Steps: 5
Number of Compounds: 5
Number of Utilities: 5
Number of Reactions: 5

Step #	Intervals
I	1
II	1
III	1
IV	1
V	1

Figure 2.7: Screenshot SUPER-O software

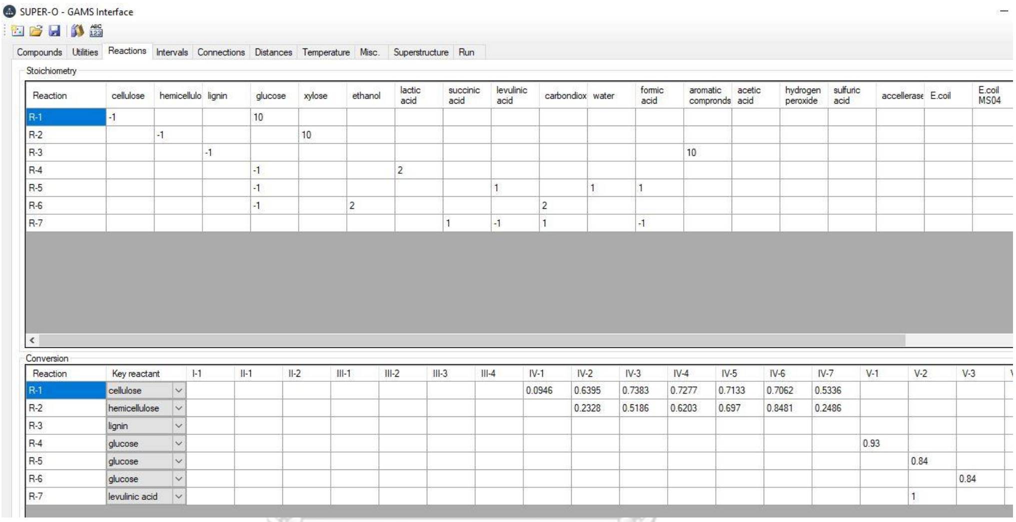
. The compounds list is required at the next step, and the utility compounds are selected through a check box. The user can edit the compound names here. For each compound, relevant physical properties are specified (molecular weight, heat capacity and enthalpy) showed in Fig. 2.8.



Name	Mw [g/mol]	Chemical Added?	Standard enthalpy [J/mol]	Heat capacity [J/mol K]
C-1	2	☐	0	0
C-2	2	☐	0	0
C-3	2	☐	0	0
C-4	2	☐	0	0
C-5	2	☐	0	0

Figure 2.8: Compounds data

The third step requires the specification of the reactions occurring in the processing network, which corresponds to the definition of stoichiometry and conversion for each of the reaction. In the stoichiometry table of the reaction tab, for each reaction, the stoichiometry is defined. SUPER-O verifies the reaction data that are specified by the user by checking the mass balance and the coherence of the defined stoichiometry. The user could also edit the reaction names here. In the conversion table, for each reaction a key reactant is chosen based on the input stoichiometry, and the reaction conversion is defined for each process interval in which the reaction takes place showed in fig.2.9.



Stoichiometry

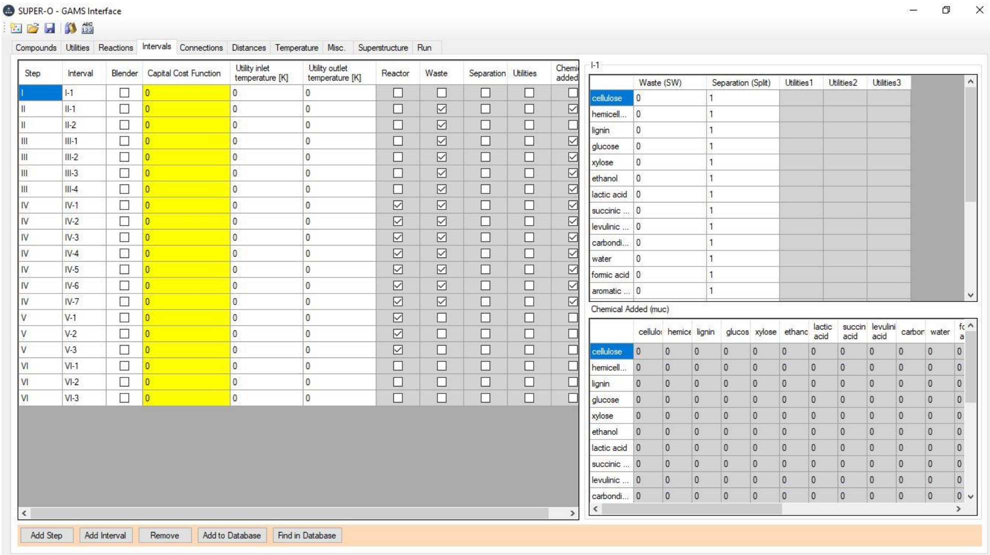
Reaction	cellulose	hemicellulo	lignin	glucose	xylose	ethanol	lactic acid	succinic acid	levulinic acid	carbondiox	water	formic acid	aromatic componds	acetic acid	hydrogen peroxide	sulfuric acid	accellerase	E.coil	E.coil MS04
R-1	-1			10															
R-2		-1			10														
R-3			-1										10						
R-4				-1			2												
R-5				-1					1		1	1							
R-6				-1		2				2									
R-7								1	-1	1		-1							

Conversion

Reaction	Key reactant	I-1	II-1	II-2	III-1	III-2	III-3	III-4	IV-1	IV-2	IV-3	IV-4	IV-5	IV-6	IV-7	V-1	V-2	V-3
R-1	cellulose								0.0946	0.6395	0.7383	0.7277	0.7133	0.7062	0.5336			
R-2	hemicellulose									0.2328	0.5186	0.6203	0.697	0.8481	0.2486			
R-3	lignin																	
R-4	glucose															0.93		
R-5	glucose																0.84	
R-6	glucose																	0.84
R-7	levulinic acid																1	

Figure 2.9: Reactions data

The fourth step of SUPER-O is related to the definition of data related to process intervals. Those include all data required for the formulation of the process model, as well as those required for the calculation of the investment cost. The interval tab is divided in 3 areas. On the left hand side, an overview of all process intervals and of their allocation to the different process steps constituting the superstructure is shown. In this section, the user can edit the intervals name, as well as specify the cost function associated to each of them (user can write mathematical expression in capital cost function cell and also the inlet and outlet of utility temperature. By clicking on the corresponding process interval, its data are displayed in the two tables on the right hand side. In the bottom part, the user can define the value of the parameter, which is used to calculate the utility consumption. In the top table, for each interval the user can define the data related to utility mixing, separation and waste production. An overview of the process tasks (utility, separation, etc.) which, based on the specified data, are active for each process interval is displayed in the form of check boxes. From the bottom tool bar, the user could add and remove an interval. Further operation of the tool bar includes save/find intervals in the database (will be available in the next version) showed in fig.2.10.



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	☐	☐	☐	☐	☐
II	II-1	☐	0	0	0	☐	☑	☐	☐	☑
II	II-2	☐	0	0	0	☐	☑	☐	☐	☐
III	III-1	☐	0	0	0	☐	☑	☐	☐	☑
III	III-2	☐	0	0	0	☐	☑	☐	☐	☑
III	III-3	☐	0	0	0	☐	☑	☐	☐	☑
III	III-4	☐	0	0	0	☐	☑	☐	☐	☑
IV	IV-1	☐	0	0	0	☑	☑	☐	☐	☑
IV	IV-2	☐	0	0	0	☑	☑	☐	☐	☑
IV	IV-3	☐	0	0	0	☑	☑	☐	☐	☑
IV	IV-4	☐	0	0	0	☑	☑	☐	☐	☑
IV	IV-5	☐	0	0	0	☑	☑	☐	☐	☑
IV	IV-6	☐	0	0	0	☑	☑	☐	☐	☑
IV	IV-7	☐	0	0	0	☑	☑	☐	☐	☑
V	V-1	☐	0	0	0	☑	☐	☐	☐	☐
V	V-2	☐	0	0	0	☑	☐	☐	☐	☐
V	V-3	☐	0	0	0	☑	☐	☐	☐	☐
VI	VI-1	☐	0	0		☐	☐	☐	☐	☐
VI	VI-2	☐	0	0		☐	☐	☐	☐	☐
VI	VI-3	☐	0	0		☐	☐	☐	☐	☐

I-1

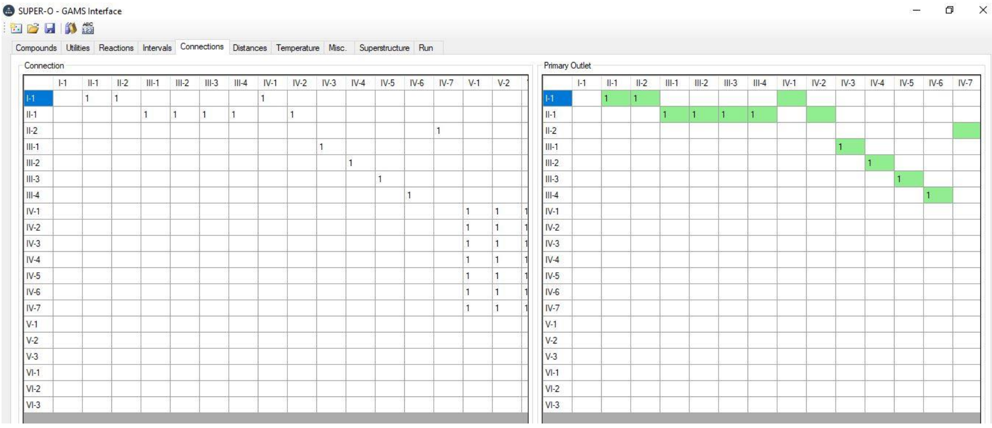
	Waste (SW)	Separation (Split)	Utilities1	Utilities2	Utilities3
cellulose	0	1			
hemicell...	0	1			
lignin	0	1			
glucose	0	1			
xylose	0	1			
ethanol	0	1			
lactic acid	0	1			
succinic ...	0	1			
levulinic ...	0	1			
carbondi...	0	1			
water	0	1			
formic acid	0	1			
aromatic ...	0	1			

Chemical Added (muc)

	cellulo	hemice	lignin	glucos	xylose	ethanc	lactic acid	succin acid	levulini acid	carbor	water	fc a
cellulose	0	0	0	0	0	0	0	0	0	0	0	0
hemicell...	0	0	0	0	0	0	0	0	0	0	0	0
lignin	0	0	0	0	0	0	0	0	0	0	0	0
glucose	0	0	0	0	0	0	0	0	0	0	0	0
xylose	0	0	0	0	0	0	0	0	0	0	0	0
ethanol	0	0	0	0	0	0	0	0	0	0	0	0
lactic acid	0	0	0	0	0	0	0	0	0	0	0	0
succinic ...	0	0	0	0	0	0	0	0	0	0	0	0
levulinic ...	0	0	0	0	0	0	0	0	0	0	0	0
carbondi...	0	0	0	0	0	0	0	0	0	0	0	0

Figure 2.10: Intervals data

In the fifth step, connectivity data are specified, by defining the possible connections between the process intervals contained in the superstructure. The visualization facilitates the definition of connection data, by clearly identifying main connections (left table of Fig.2.11) and bypasses (green cells of right table of Fig.2.11). Moreover, transportation data (Fig.2.12) and stream temperature (Fig.2.13) are also specified within this step. To facilitate this task, since transportation and stream temperature can be specified only if connections are existing, SUPER-O highlights the existing connections in green for the user to input the data.



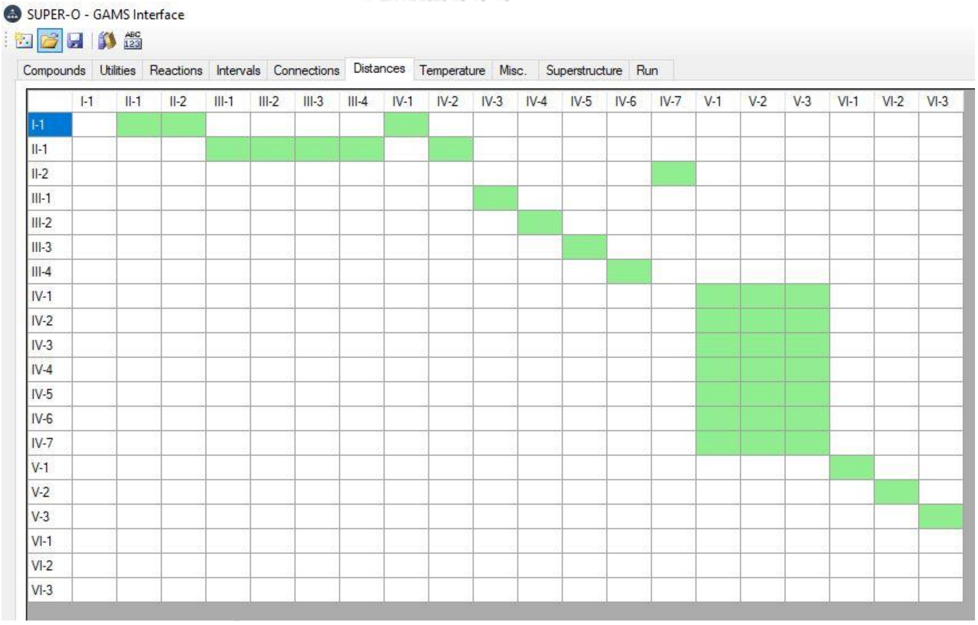
Connection

	I-1	II-1	II-2	III-1	III-2	III-3	III-4	IV-1	IV-2	IV-3	IV-4	IV-5	IV-6	IV-7	V-1	V-2
I-1		1	1					1								
II-1				1	1	1	1		1							
II-2														1		
III-1										1						
III-2											1					
III-3												1				
III-4													1			
IV-1															1	1
IV-2															1	1
IV-3															1	1
IV-4															1	1
IV-5															1	1
IV-6															1	1
IV-7															1	1
V-1																
V-2																
V-3																
VI-1																
VI-2																
VI-3																

Primary Outlet

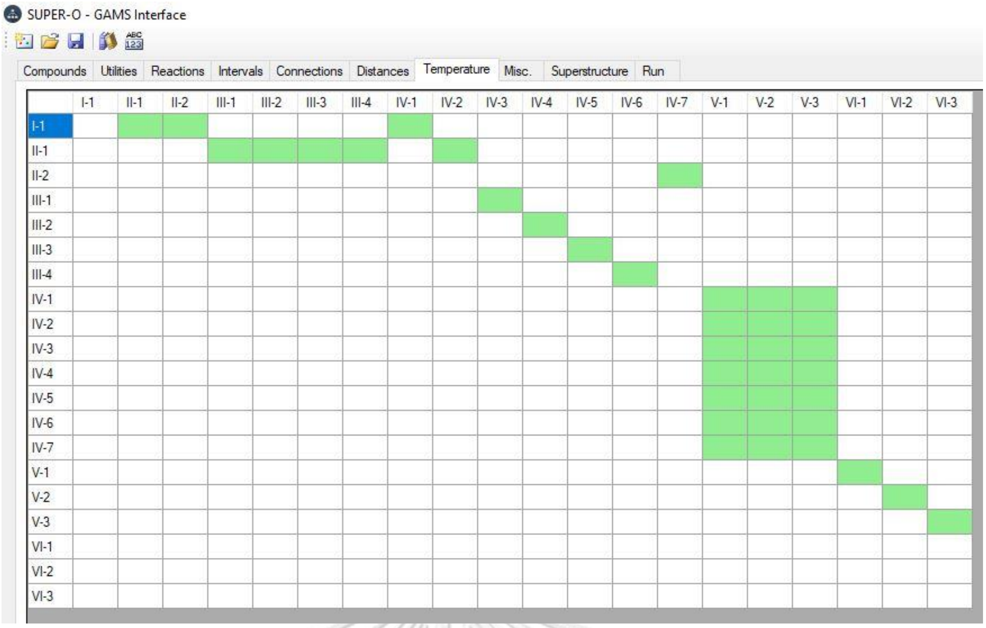
	I-1	II-1	II-2	III-1	III-2	III-3	III-4	IV-1	IV-2	IV-3	IV-4	IV-5	IV-6	IV-7
I-1		1	1					🟩						
II-1				1	1	1	1		🟩					
II-2														🟩
III-1										1				
III-2											1			
III-3												1		
III-4													1	
IV-1														
IV-2														
IV-3														
IV-4														
IV-5														
IV-6														
IV-7														
V-1														
V-2														
V-3														
VI-1														
VI-2														
VI-3														

Figure 2.11: Connects data



	I-1	II-1	II-2	III-1	III-2	III-3	III-4	IV-1	IV-2	IV-3	IV-4	IV-5	IV-6	IV-7	V-1	V-2	V-3	VI-1	VI-2	VI-3
I-1		🟩	🟩					🟩												
II-1				🟩	🟩	🟩	🟩		🟩											
II-2														🟩						
III-1										🟩										
III-2											🟩									
III-3												🟩								
III-4													🟩							
IV-1															🟩	🟩	🟩			
IV-2															🟩	🟩	🟩			
IV-3															🟩	🟩	🟩			
IV-4															🟩	🟩	🟩			
IV-5															🟩	🟩	🟩			
IV-6															🟩	🟩	🟩			
IV-7															🟩	🟩	🟩			
V-1																		🟩		
V-2																			🟩	
V-3																				🟩
VI-1																				
VI-2																				
VI-3																				

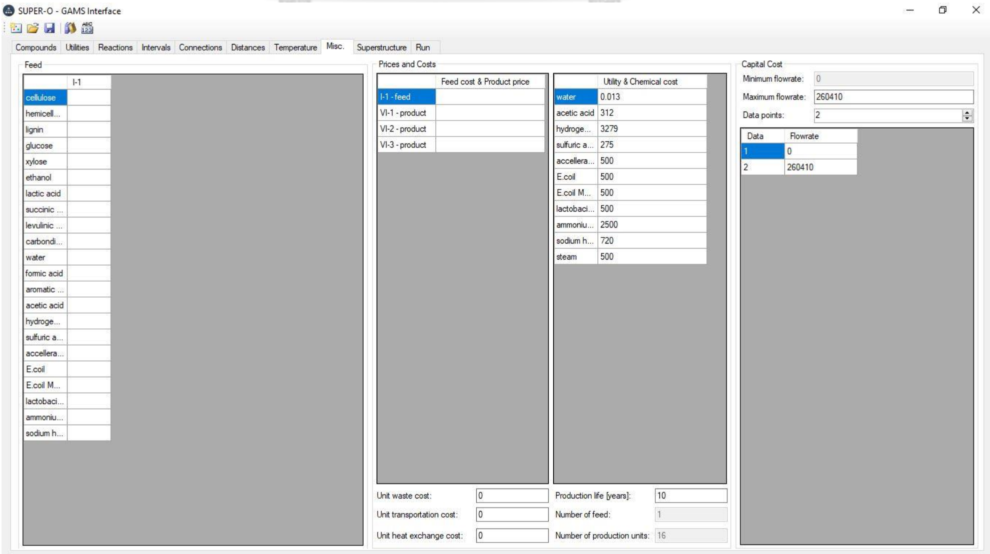
Figure 2.12: Distances data



	I-1	II-1	II-2	III-1	III-2	III-3	III-4	IV-1	IV-2	IV-3	IV-4	IV-5	IV-6	IV-7	V-1	V-2	V-3	VI-1	VI-2	VI-3
I-1		🟩	🟩					🟩												
II-1				🟩	🟩	🟩	🟩		🟩											
II-2														🟩						
III-1										🟩										
III-2											🟩									
III-3												🟩								
III-4													🟩							
IV-1															🟩	🟩	🟩			
IV-2															🟩	🟩	🟩			
IV-3															🟩	🟩	🟩			
IV-4															🟩	🟩	🟩			
IV-5															🟩	🟩	🟩			
IV-6															🟩	🟩	🟩			
IV-7															🟩	🟩	🟩			
V-1																		🟩		
V-2																			🟩	
V-3																				🟩
VI-1																				
VI-2																				
VI-3																				

Figure 2.13: Temperature data

The last step of the data structure is concerned with the definition of miscellaneous data. At the present stage of development of SUPER-O, this corresponds to the feed composition, utility cost, raw material/product price, penalty for waste emission, unit heat cost, production life and setup of the piecewise linearization of the capital cost constraints showed in fig.2.14.



	I-1
cellulose	
hemicell...	
lignin	
glucose	
xylose	
ethanol	
lactic acid	
succinic ...	
levulinic ...	
carbondi...	
water	
formic acid	
aromatic ...	
acetic acid	
hydroge...	
sulfuric a...	
accellera...	
E.coil	
E.coil M...	
lactobaci...	
ammoniu...	
sodium h...	

	Feed cost & Product price
I-1 - feed	
VI-1 - product	
VI-2 - product	
VI-3 - product	

	Utility & Chemical cost
water	0.013
acetic acid	312
hydroge...	3279
sulfuric a...	275
accellera...	500
E.coil	500
E.coil M...	500
lactobaci...	500
ammoniu...	2500
sodium h...	720
steam	500

Unit waste cost: 0
Unit transportation cost: 0
Unit heat exchange cost: 0

Production life [years]: 10
Number of feed: 1
Number of production units: 16

Minimum flowrate: 0
Maximum flowrate: 260410
Data points: 2

Data	Flowrate
1	0
2	260410

Figure 2.14: Miscellanea data

When the problem specification steps are completed, the superstructure resulting from this formulation is visualized. The visualization of the superstructure is generated based on the intervals data and the connectivity data, and automatically shown in SUPER-O.

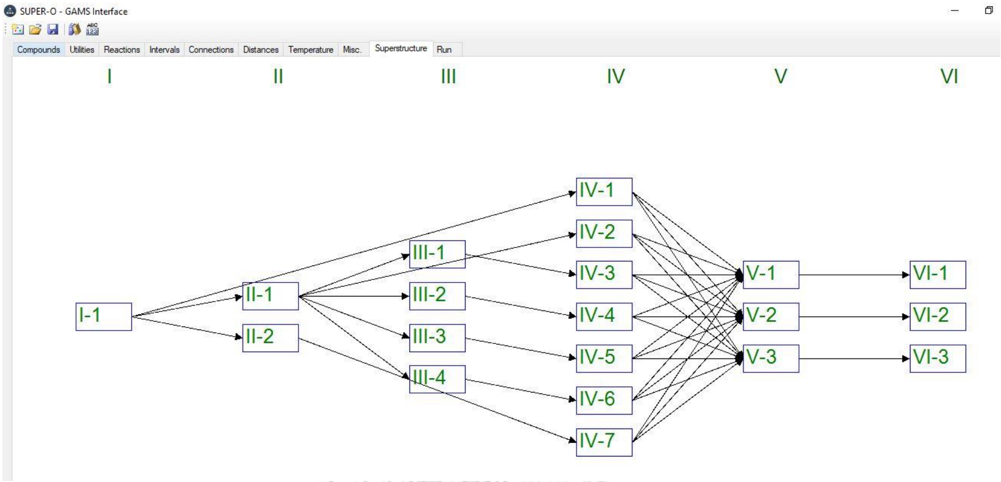


Figure 2.15: Superstructure visualization

When collecting data to create the superstructure, then the data is processed according to the objective function to find the result with GAMS.

2.9 GAMS integration

When the problem specification is saved, the corresponding excel file and gdx file of the project are generated. The user could choose the input excel file for optimization (when the project is saved or loaded, the default input excel file is selected automatically according to the user's option). The user could also choose the GAMS templates for the project.

2.10 Literature review

Mongkhonsiri et al. (2018) studied developing sustainable processes for pulp and paper industry by integration of the biorefinery concept to an existing pulp and paper process showed in fig.2.16. Superstructure optimization was performed with the objective function to maximize profit to determine optimal integrated networks for three scenarios. The obtained results provided useful insights for further development of the optimal networks as sustainable integrated biorefinery combined with pulp and paper mills. 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.

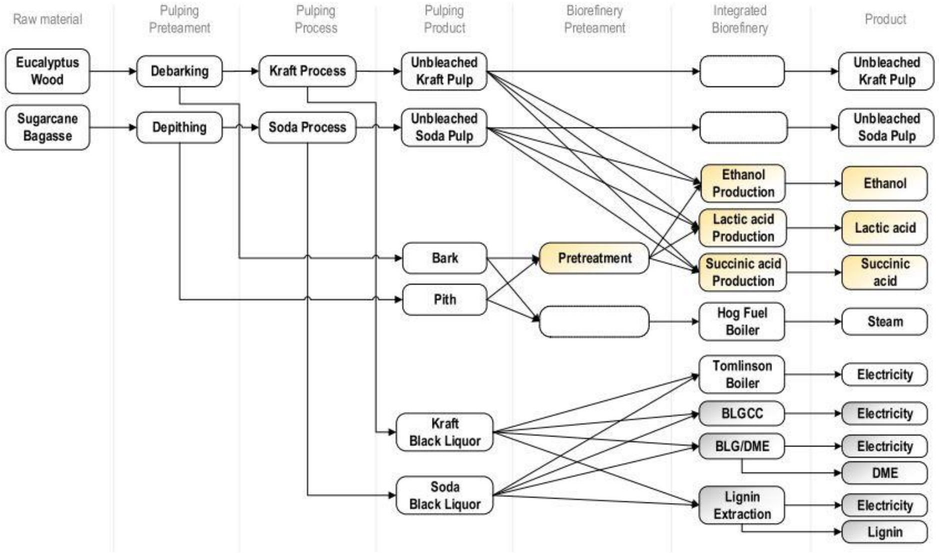


Figure 2.16: Overview of superstructure for integrated biorefinery network

Rizwan et al. (2015) revealed that microalgae had great potential as a feedstock for the production of a wide range of end-products under the broad concept of biorefinery and propose a superstructure (showed in fig.2.17) based optimization model to find the optimal processing pathway for the production of biodiesel from microalgal biomass, and identified several challenges with the focus being on utilizing lipids extracted microalgal biomass for economic and environmentally friendly production of useful energy products. The results showed that the GOM (Sales - Operating Cost) lied below the breakeven point, and hence the production of microalgal biofuels was not economically viable. Economic sensitivity analysis revealed the parameters that should be targeted for substantial improvements in the economics of microalgae-derived fuels. That must be handled in the future by technical breakthroughs from both engineering and biological perspectives of microalgae.

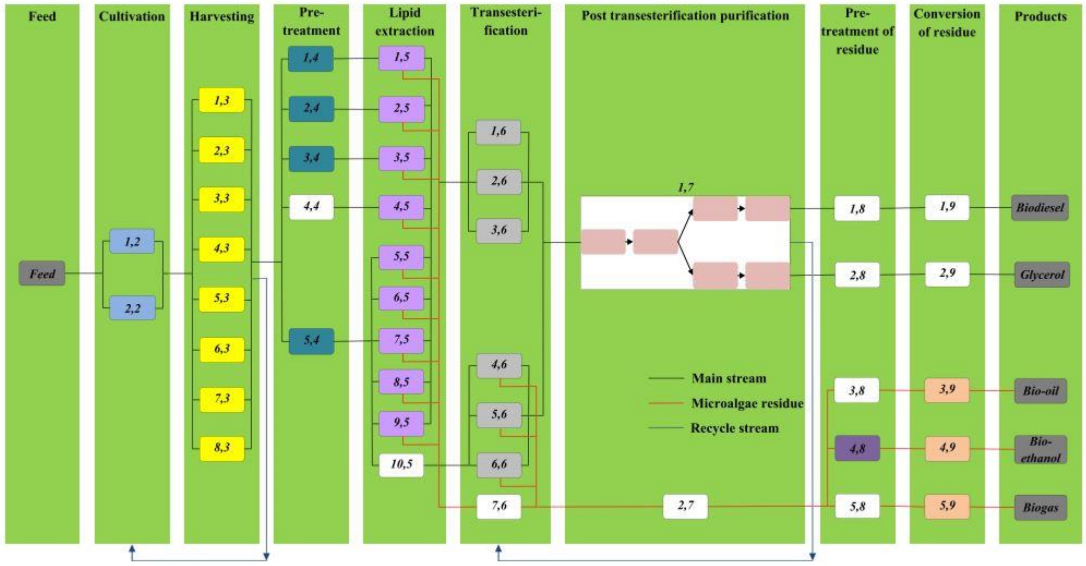


Figure 2.17: Biorefinery superstructure for the production of biofuels from C.vulgaris

Kongpanna et al. (2016) studied a systematic computer-aided framework for sustainable process design was presented together with its application to the synthesis and generation of processing networks (showed in fig.2.18) for dimethyl carbonate (DMC) production with CO_2 utilization. From the result, the product was DMC, and to produce it, CO_2 must be used as a feedstock. Therefore, information on all known technologies where CO_2 may be used to produce DMC is necessary.

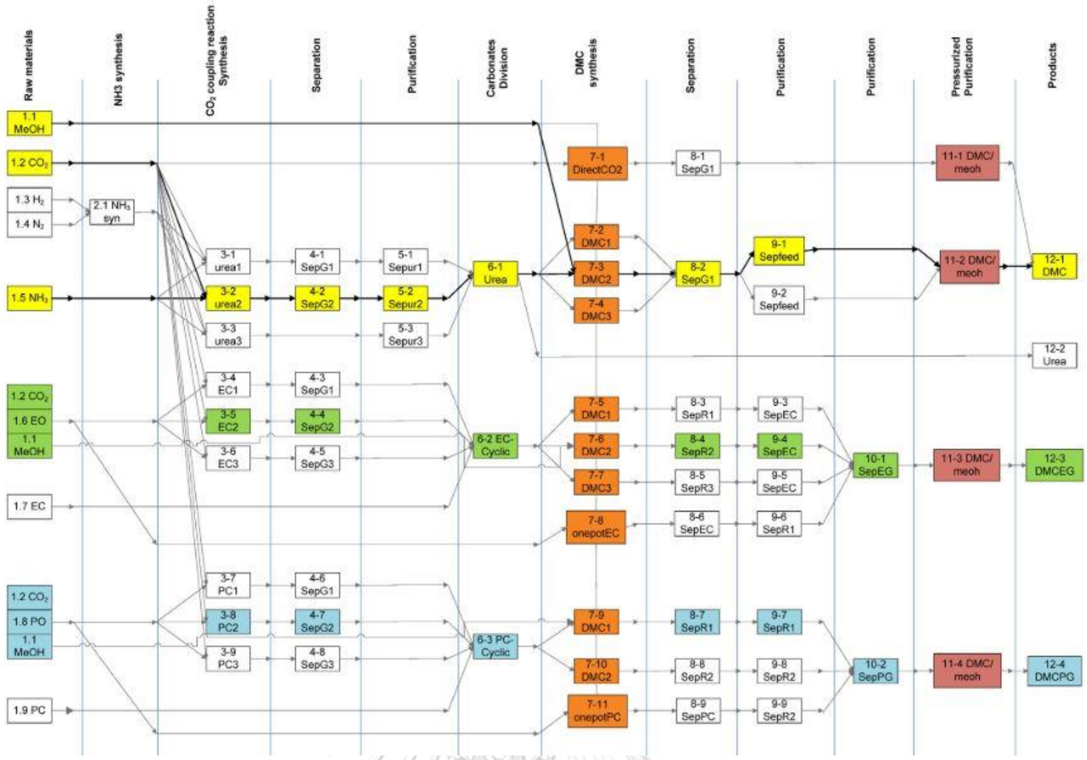


Figure 2.18: Superstructure for DMC production network highlighting the optimal processing steps

De Faria et al. (2014) studied a systematic method for synthesis and analysis of biomass based biorefinery pathways (process networks showed in fig 2.19) in terms of current and future market conditions. The systematic method had been implemented into a computer aided tool that was able to quickly evaluate alternatives and network scenarios. The tool integrates data collection, modelling and superstructure optimization to determine the optimal network for a biorefinery. The problem of biorefinery design had been formulated and solved, leading to the identification, for the present market scenario, of the optimal biorefinery configuration along with its optimal product portfolio: glycerol, 12-HSA, HCO, undecylenic acid, heptaldehyde, 2-octanol, sebacic acid and ricinoleic acid.

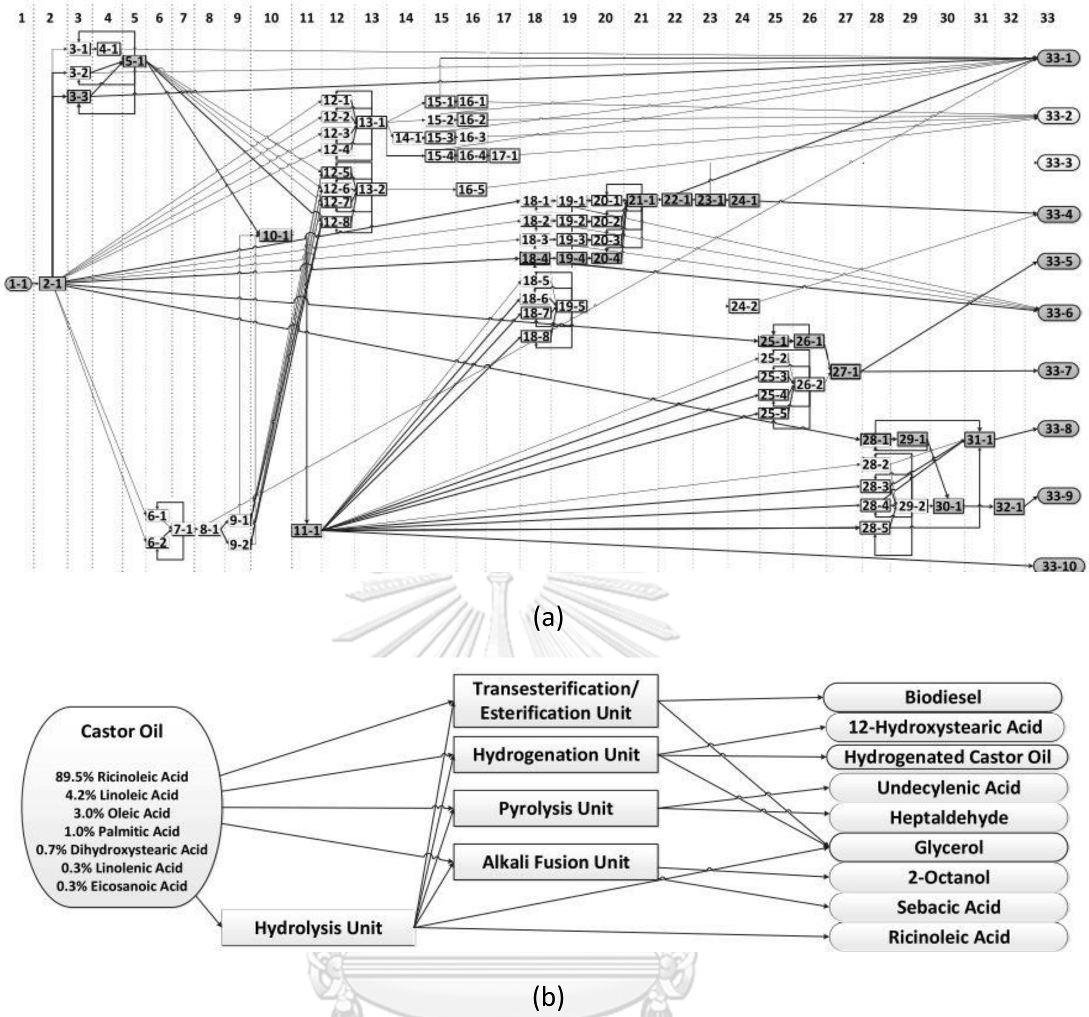


Figure 2.19: a. Biorefinery superstructure with optimal flowsheet selected (the filled boxes in grey) and b. Biorefinery flow diagram

Chapter 3

Methodology

The research methodology for conversion of palm biomass into various value-added products via different available conversion technologies of palm empty fruit bunches in Thailand consists of four stages. These include 1) a stage of defining problem 2) a superstructure generation 3) changing the superstructure into mathematical model and 4) mathematical optimization as shown in Figure 3.1. The optimization is performed subject to the user-defined objective functions such as profit maximization, minimization of the cost of operation and utility and etc.. Please also note that there exist other factors and limitations that depend upon the production process and the utilized unit operations. These constraints must be considered also in the optimization of the superstructure.

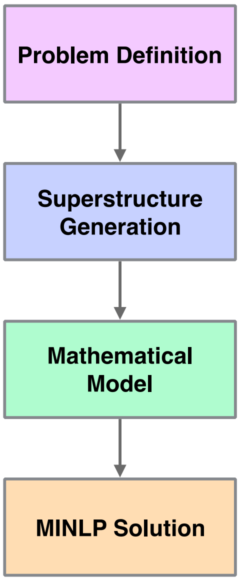


Figure 3.1: Process methodology framework

3.1 Problem definition (Step 1)

In this step the problem must be specified and clearly established. In this work, the problem associates with the use of palm biomass that is still inefficient and ineffective specifically the empty fruit bunch that is abundant and readily available during the process of collections of palm fruits. By considering the useful constituents in the biomass that contains lignocellulosic network, the sugar monomer such as glucose can be obtained from the proper processing of biomass. The steps of the biomass processing involve the pretreatments, the hydrolysis and the fermentation. According to the discussions provided in Chapter 2, each processing step has multiple types of methods, i.e., physical, chemical and biological pretreatments. Thus, in order to determine the most optimal route for the processing of the biomass from palm, all alternatives and their crucial information must be compiled. The critical pieces of information are the mass balance and the utility usage in each processing block. Please note that the feedstock and the value-added product in this work will be narrowed down to the empty fruit bunch and ethanol respectively. The variations of the feedstock and the value-added products will be studied in the future work.

3.2 Superstructure Generation (Step 2)

In this research, the superstructure of possible alternatives of the processing steps is generated based on the compiled information mentioned in Section 3.1. The processing steps, e.g., pretreatments, hydrolysis and fermentation are clearly defined. In each processing step, the variations are listed. For example, in the processing step of pretreatment, the physical, the chemical and the biological pretreatments will be listed. After the superstructure is generated, the corresponding mass balance as well as the utility usage information obtained from previous experiments or literature will be provided in each processing block. All configurations will be pre-screened by the market trend of Thailand. The configurations that are inconsistent with the specified constraints will be eliminated from the superstructure. Figure 3.2 provides the example of the expected superstructure. The pretreatment, the hydrolysis and the fermentation are defined as steps 1, 2 and 3 as depicted in the figure.

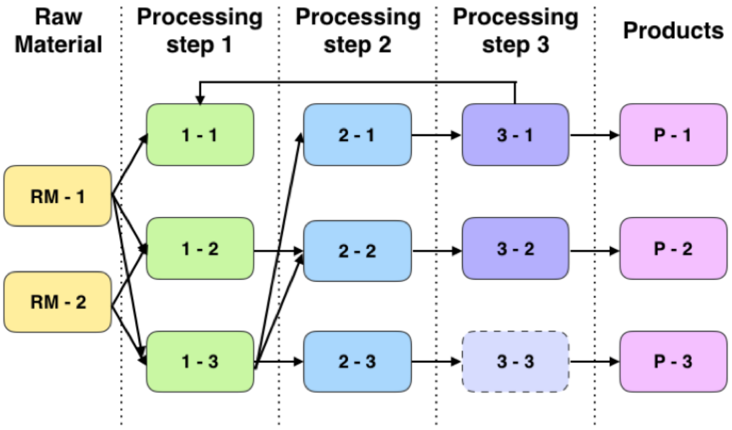


Figure 3.2: Representation of Processing Step-Interval Network (PSIN) (Bertran et al., 2017)

3.3 Mathematical Model (Step 3)

A mathematical model is developed and validated to represent the obtained superstructure in Section 3.2. Each process interval is represented by the mathematical models using the pieces of information of mass and energy balances. The mathematical programming problem, process constraints and the variable bounds will be formulated in terms of MILP or MINLP problems. The consistency of the model and the data will be checked that the collected data include all the model parameter values. The superstructure is linked with the list of decision variables. The superstructure generation can be performed by specific software such as SuperO (Bertran et al., 2017).

3.4 MILP and MINLP Solution (Step 4)

The formulated MILP and MINLP problems from Step 3 can be solved with optimization program such as GAMS. An optimal processing pathway of the empty fruit bunch that satisfies the specified objective function will be determined by the optimization of the superstructure. Further, variations of the optimal solutions are expected as the objective functions vary depending upon the need and the geological context where the biomass is obtained.

Chapter 4

Results and discussion

4.1 Problem definition

In this stage, defining the problem is undertaken firstly. According to literature review, the main product obtained from palm mill is palm oil extracted from fresh fruit of palm. The biomass remains low value and hard to dispose of in the process is mostly the empty fruit bunch. Attempts to utilize the empty fruit bunch to produce higher value products (ethanol, succinic acid and lactic acid) are more popularly. The main steps to convert the empty fruit bunch to higher value products consist of pretreatment, hydrolysis and fermentation.

4.2 Superstructure Generation

The superstructure is generated in this stage. Data from literature for construction of the superstructure require amounts of chemicals used in each processing block for mass balance calculations.

Shamsudin et al. (2012) studied the effect of steam pretreatment on empty fruit bunch of palm to produce sugars. The mass balance is undertaken using data from this research. According to the data, the pretreatment using steam can recover cellulose nearly 100% with the removal of lignin at 20% with respect to the empty fruit bunch mass. Next, the cellulose is fed to the hydrolysis process to convert 26% of cellulose to sugar.

Palamae et al. (2017) studied the effect of chemical pretreatment on empty fruit bunch of palm. This research compared the feed ratio of the chemical used in the process including a sequential two-step treatments with peracetic acid (PA) and alkaline peroxide (AP) at mild temperatures (20–35 degree Celsius). According to this research, more than 98 percentage of the lignin was removed from palm empty fruit bunch (EFB). This result is also used in the mass balance calculation.

El Fergani et al. (2017) studied the production of succinic acid from glucose using Nb (0.02 and 0.05 moles percentage)-Beta zeolites obtained by a post-synthesis methodology. Therefore, at 180 degree Celsius, 18 bar O_2, and 12 hours reaction time, the oxidation of glucose occurred with a selectivity to succinic acid as high as 84 percentage for a nearly 100% conversion.

Moon et al. (2012) studied the production of lactic acid from glucose with bacterium, Lactobacillus paracasei subsp. paracasei CHB2121 in fermentation process. The research revealed that the purity of the produced lactic acid was estimated to be 96.6% of lactic acid with 94% conversion.

Parra-Ramírez et al. (2018) studied the technical and economic potential evaluations of the strain Escherichia coli MS04 in the ethanol production from glucose. According to the result, it is highlighted that the initial concentration of biomass only affects the fermentation time. 84% conversion of glucose to ethanol is attained from this work.

The results obtained from the literature mentioned above were used in the superstructure development as shown in Fig. 4.1. The developed superstructure consists of six major processing steps/stages:

1. feed stock of empty fruit bunches
2. pretreatment,1 (chemical pretreatment such as peracetic acid or physical pretreatment such as steam explosion)
3. pretreatment,2 (alkaline peroxide)
4. hydrolysis process
5. fermentation
6. products (ethanol, succinic acid and lactic acid)

At each processing stage, a number of technological alternatives/options are modeled to perform the respective task. As shown in Fig. 4.1, each in the superstructure is represented by two indexes. First index represents option in process and second index represents physical description of all options in processing steps. These processing steps are included in the superstructure that connects the upstream (e.g. the empty fruit bunches) to the downstream (i.e. the value-added chemicals such as lactic acid, succinic acid and bioethanol). This superstructure model are given in Table 4.1.

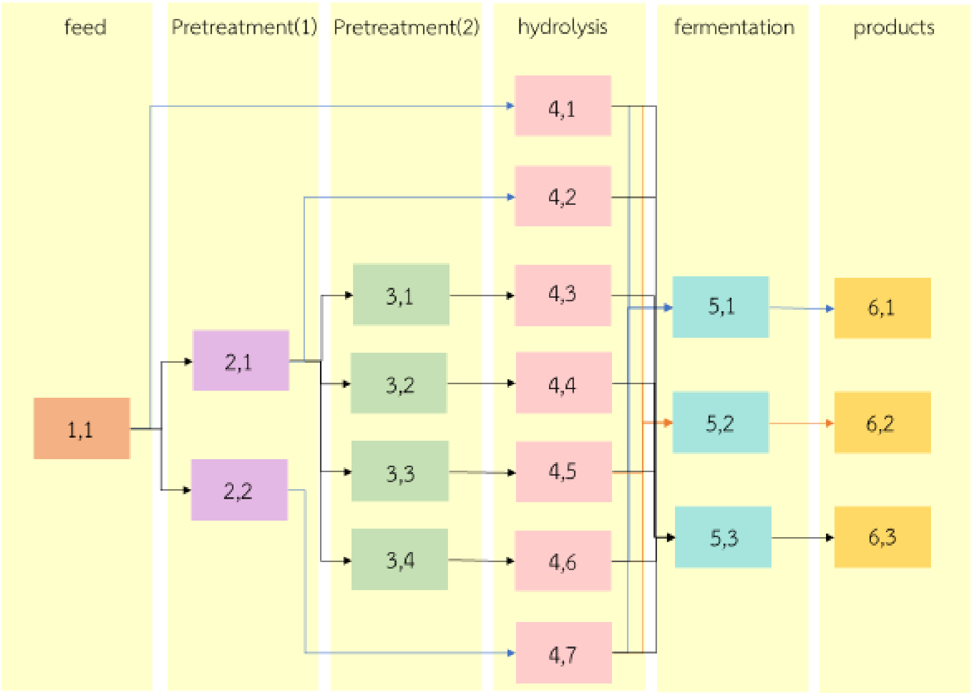


Figure 4.1: Superstructure development of lignocellulosic biomass from empty fruit bunch of palm

Superstructure optimization is performed to determine optimal integrated networks of three products (lactic acid, succinic acid and bioethanol). 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 kilogram per year of raw material used and considered with 10 years of project life. Raw material and product prices used in the calculations for all scenarios are given in Table 4.1

Table 4.1: List of processing alternatives/options and their references.

Box.	Technological alternative/option	data	Reference
1,1	Feed empty fruit bunches 1000kg	Fraction in EFB - cellulose 0.283 - hemicellulose 0.366 - lignin 0.351	Palamae et al. (2017), Linde et al. (2008)
2,1	Chemical pretreatment (peracetic acid)	Fraction - cellulose 0.444 - hemicellulose 0.392 - lignin 0.164	Palamae et al. (2017)
2,2	Physical pretreatment (steam explosion)	Fraction - cellulose 0.344 - hemicellulose 0.316 - lignin 0.339	Shamsudin et al. (2012)
3,1	Pretreatment (alkaline peroxide) with condition 20°C, 4% NaOH	Fraction - cellulose 0.853 - hemicellulose 0.118 - lignin 0.029	Palamae et al. (2017)
3,2	Pretreatment (alkaline peroxide) with condition 40°C, 4% NaOH	Fraction - cellulose 0.865 - hemicellulose 0.099 - lignin 0.036	Palamae et al. (2017)
3,3	Pretreatment (alkaline peroxide) with condition 20°C, 8% NaOH	Fraction - cellulose 0.883 - hemicellulose 0.088 - lignin 0.029	Palamae et al. (2017)
3,4	Pretreatment (alkaline peroxide) with condition 40°C, 8% NaOH	Fraction - cellulose 0.892 - hemicellulose 0.072 - lignin 0.036	Palamae et al. (2017)
4,1	Hydrolysis	Fraction - glucose 0.189 - xylose 0.810 - other 0	Sindhu et al. (2016), Palamae et al. (2017)
4,2	Hydrolysis	Fraction	Sindhu et al. (2016),

		- glucose 0.631 - xylose 0.297 - other 0.071	Palamae et al. (2017)
4,3	Hydrolysis	Fraction - glucose 0.907 - xylose 0.088 - other 0.004	Sindhu et al. (2016), Palamae et al. (2017)
4,4	Hydrolysis	Fraction - glucose 0.826 - xylose 0.080 - other 0.004	Sindhu et al. (2016), Palamae et al. (2017)
4,5	Hydrolysis	Fraction - glucose 0.759 - xylose 0.074 - other 0.004	Sindhu et al. (2016), Palamae et al. (2017)
4,6	Hydrolysis	Fraction - glucose 0.718 - xylose 0.070 - other 0.004	Sindhu et al. (2016), Palamae et al. (2017)
4,7	Hydrolysis	Fraction - glucose 0.7 - xylose 0.3	Sindhu et al. (2016), Shamsudin et al. (2012)
5,1	Fermentation with Lactobacillus paracasei	93% conversion	Moon et al. (2012)
5,2	Fermentation of glucose with Nb-based zeolites catalyst	84% conversion	El Fergani et al. (2017)
5,3	Fermentation with Escherichia coli MS04	84% conversion	Parra-Ramírez et al. (2018)

Table 4.2: Raw material and product price for superstructure optimization

Raw material/Products	Price ($/ton)	Reference
Empty fruit bunces	29	Ooi et al. (2017)
Lactic acid	2300	Lee (2015)
Succinic acid	3000	Lee (2015)
Bioethanol	769	Bertran et al. (2017)

After creating superstructure, next step will be determination of alternatives that are consistent with objective functions based on mathematics model.

4.3 Mathematics model

A set of mathematical models is developed and validated to represent the superstructure. The generic modelling approach that has proposed in several case studies in process synthesis problems 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. From the theoretical equations in appendix, the objective function was changed by reducing the terms of utility and capital costs. This was undertaken because the terms utility and capital cost could not be determined since the shipping cost and the price of equipment were not provided. The remaining equations are as follows:

Objective function

$$Max\ Z = \sum_{i}\sum_{k} P_{k}^{P} f_{i,k}^{W} - \sum_{i}\sum_{kk} P_{kk}^{RW} f_{i.kk}^{W} - \sum_{kk}\sum_{i} P_{i}^{C} g_{i.kk}^{M}$$

4.4 Results and discussion

The proposed modeling framework is implemented to determine the most optimal processing pathways specific to the selected chemicals.

4.4.1 Scenario 1: Maximization of profit

A summary of the mathematics model along with solution statistics is given in Appendix. The optimal processing pathway showed in Fig. 4.2 determined for this scenario is slightly different as it consists of pretreatment, hydrolysis and fermentation. The results showed that route in Fig. 4.2 is the most profitable with the highest profits of 6404000 dollars/year accounting for 89% profit relative to the raw material cost - the raw material and reactive chemicals are 29000 and 776000 dollars/year respectively. From these results, the route that produces succinic acid returns the higher profit than lactic acid and bioethanol. Therefore, it can be concluded that the identification of the most optimal processing pathways subject to the maximization of profit reveals the production of succinic acid

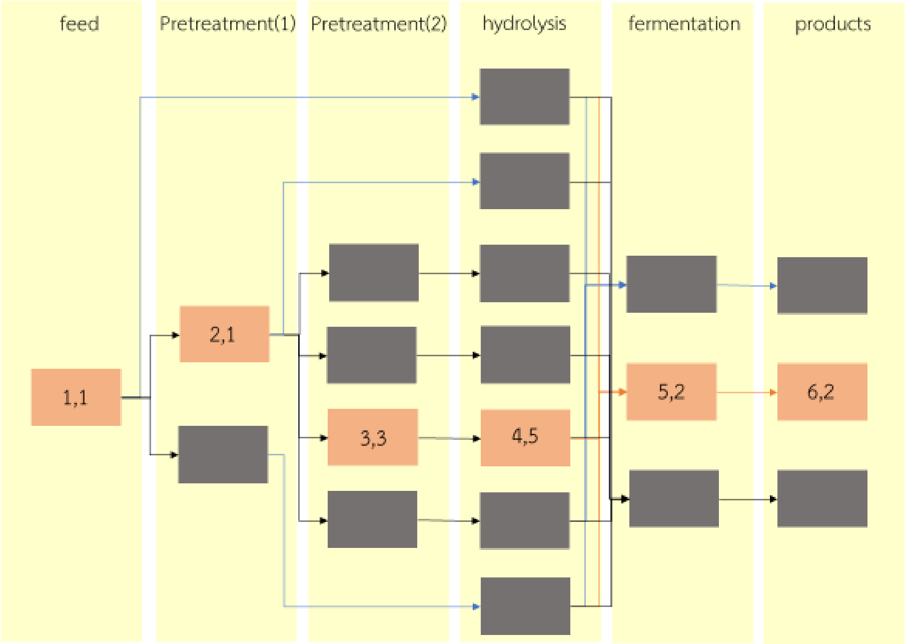


Figure 4.2: The superstructure showing the network of processing routes to produce chemical product from empty fruit bunches of oil palm. In this figure, the processing route selected from the optimization is highlighted.

4.4.2 Scenario 2: Optimal processing route specific for each chemical

In the mechanism of the market economy, consumers make purchasing decisions based on the maximum utility optimization whereas manufacturers make marketing decisions based on the principles of increasing profits. Between supply and demand, the market suggests resources to efficiently allocate resources based on natural fluctuations in prices. The market is like 'Invisible Hand' which drives manufacturers and consumers to make sequential decisions under the collaboration of price mechanisms, supply and demand mechanisms and competition mechanisms (Wu, 2011). Therefore, the most profitable production of these chemicals (lactic acid, succinic acid and bioethanol) will change according to the market mechanism. In this scenario study, finding the most suitable route to produce lactic acid, succinic and bioethanol is focused. The results are shown in Tables 4.3, Fig.4.3, 4.4 and 4.5 respectively**.**

Table 4.3 shows prices of raw material, chemical added, sales, profits and percentage of profit of the best routes to produce lactic acid, succinic acid and bioethanol. According to the results, the processing pathways for the production of succinic acid, lactic acid and bioethanol are provided in Figs. 4.3, 4.4 and 4.5. Further, as seen from this Table 4.3, succinic acid yields the highest profit which is consistent with the result obtained in Scenario 1.

Table 4.3: Optimization result on scenario 2

Products	**Price ($/year)**				**Percentage of profit**
	Raw material	**Chemical added**	**Sale**	**Profit**	
Lactic acid	29000	775400	5510000	4705000	85
Succinic acid	29000	776000	7210000	6404000	89
bioethanol	29000	776000	1840000	1039000	56

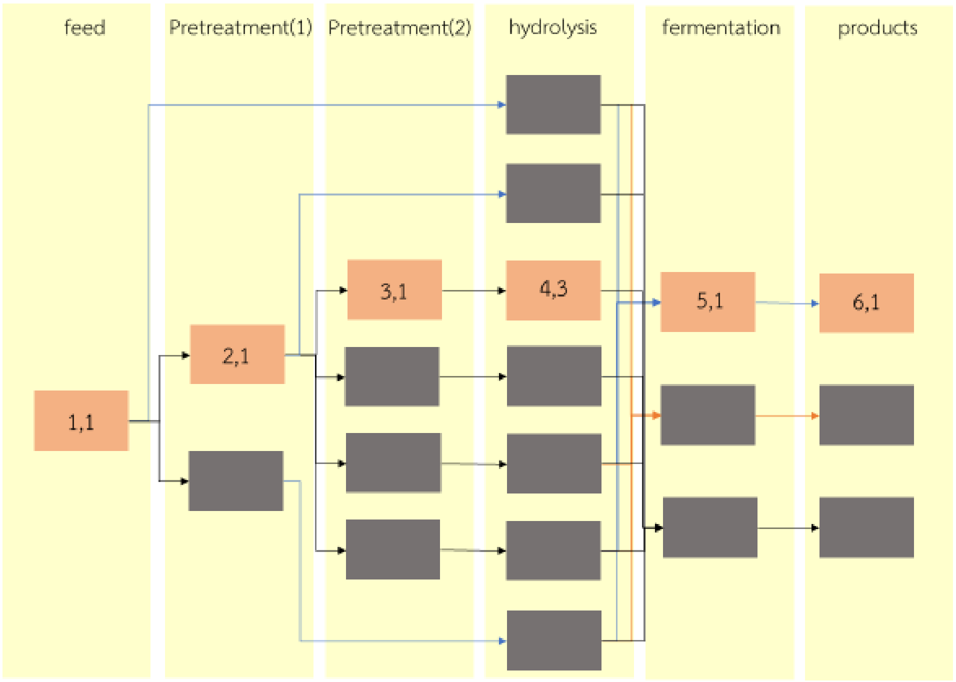


Figure 4.3: The superstructure showing the best route to produce lactic acid from empty fruit bunches of oil palm

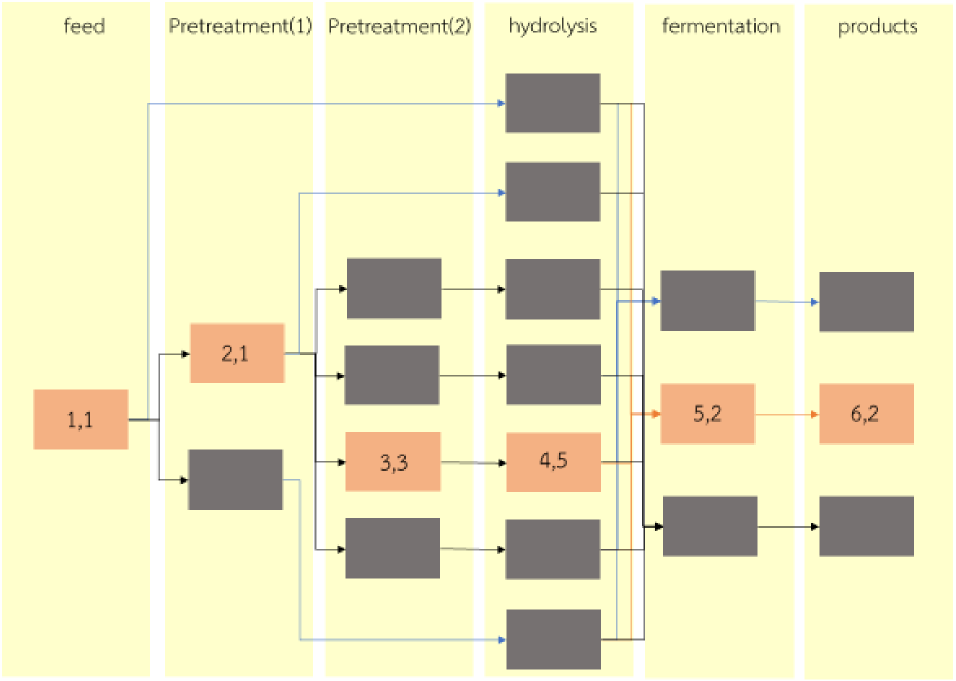


Figure 4.4: The superstructure showing the best route to produce succinic acid from empty fruit bunches of oil palm

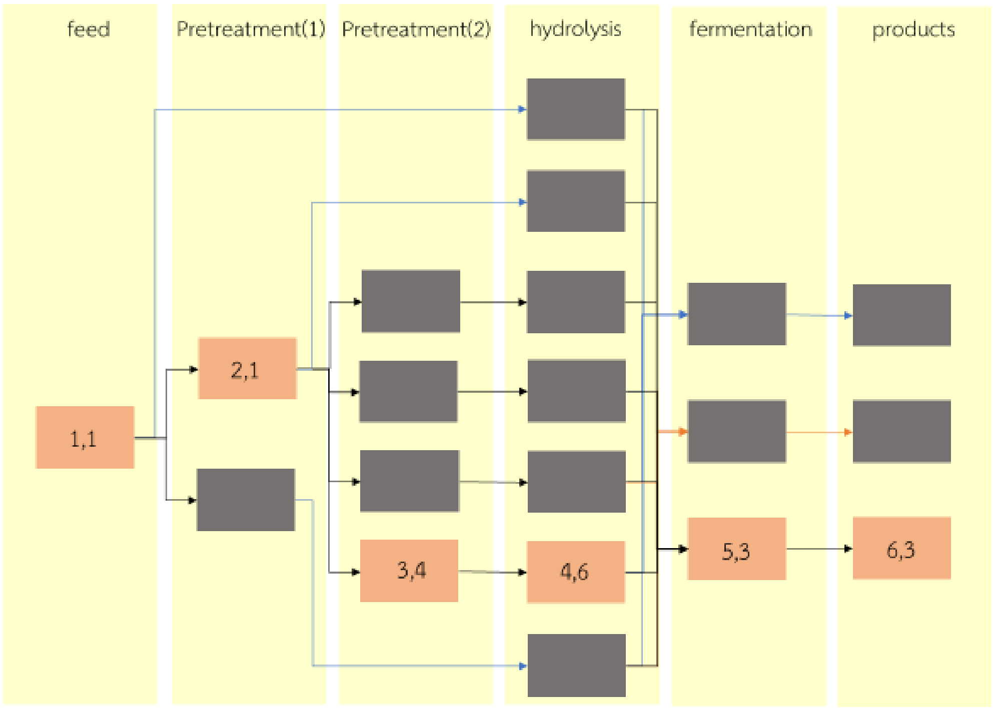


Figure 4.5: The superstructure showing the best route to produce bioethanol from empty fruit bunches of oil palm

4.4.3 Scenario 3: Various chemical product prices between succinic acid and lactic acid

According to the Scenarios 1 and 2, the products in the superstructure optimization that show the highest potential are lactic acid and succinic acid. Further, productions of these chemicals have gained interests because these chemicals are used as a precursor for the productions of biodegradable plastics, food industry. Because of this, the value in the market as well as the demand for this chemicals are increasing, which has boosted the production scale of succinic acid and lactic acid.

Succinic has various applications in industry due to its special functions. It is widely used as a surfactant, detergent extender, foaming agent, and ion chelator in plating and antimicrobial agent (Du et al., 2015).

Due to lactic acid is the most widely investigated carboxylic acid from natural resources, and it has achieved widespread, successful commercialization. Industrially, lactic acid is an important chemical that is used as a precursor of valuable compounds, such as propylene glycol and acrylic polymers (Castillo Martinez et al., 2013).

In this scenario, sensitivity of the chemical prices that would result in the more profitable production of lactic acid than succinic acid was undertaken. According to Tables 4.1 and 4.2, the route that produces lactic acid yields 85% compared to 89% from the succinic production. It is found in the sensitivity analysis that the production of lactic acid can be more profitable than the production of succinic acid if only the lactic acid cost was greater or equal to the succinic acid as given in Table 4.4.

Table 4.4: Optimization result on scenario 3

Products	Price ($/year)				Percentage of profit
	Raw material	Chemical added	Sale	Profit	
Lactic acid	29000	775400	5509500	4705000	85
Succinic acid	29000	776000	7209000	6404000	89
Lactic acid (when price equal to succinic)	29000	754000	7210000	6427000	89

Chapter 5

Conclusions

In conclusion, an MINLP model is developed to determine optimal/promising configurations from a large number of processing alternatives for the process of adding value to the empty fruit bunches of palm oil. From the results, top value-added biochemicals have been identified as succinic acid (89% profit) which is superior to lactic acid and ethanol. In addition, the pathways of productions (lactic acid, succinic acid and bioethanol) will change according to the market mechanism leading to the different production alternatives. The last one is the comparison of 2 chemical products (lactic acid and succinic acid) suggesting that if the lactic acid price is more than or equal to the succinic acid, the selection path will shift to lactic acid. The superstructure of the adding value process to the empty fruit bunches of palm oil can be used for process development in the future.

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 the process of adding value to the empty fruit bunches of palm oil. 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.

Appendix

Mathematical Model

Next step, mathematical model. A set of mathematical models has been developed and validated to represent superstructure. The general modeling methods proposed in many cases are studied in the process synthesis problem be used in this work. Each period of the process is represented by a general mathematical model. The process duration model is determined in terms of component mass balance and energy balance. The group of processing processes is the mixing of chemical inlet, reaction, waste separation, product separation and utility for each processing time. A schematic representation of the generic process interval with representing mass flowrate variables is shown in Fig. A.1. 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. 1–22 (Quaglia et al., 2015) The consistency of model and data is checked and it is verified that the collected data represents

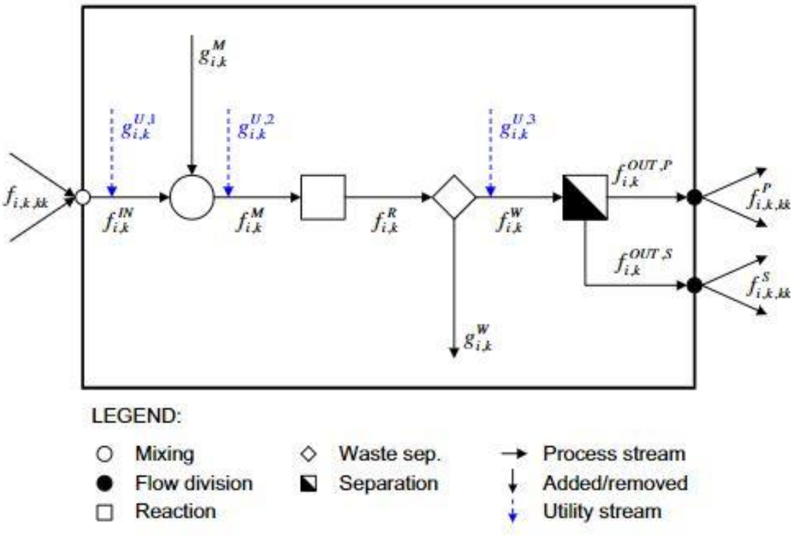


Figure A.1: The generic process interval with internal variables (Bertran et al., 2017)

Mathematical model of superstructure optimization

Objective function

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

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

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

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

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

$$f_{i,kk}^{OUT,P} = f_{i,kk}^{W}\sigma_{i,kk} \qquad (10)$$

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

Superstructure logical constraint

$$f_{i,k,kk}^{2} \leq f_{i,k}^{OUT,S}\left(S_{k.kk} - SP_{i,kk}\right) \qquad (13)$$

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

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

$$f_{i,k,kk}^{1} \leq f_{i,kk}^{OUT,P} SP_{k,kk} \qquad (16)$$

$$f_{i,k,kk} = f_{i,k,kk}^{1} + f_{i,k,kk}^{2} \qquad (17)$$

$$f_{i,kk}^{IN} = \sum_{k} f_{i.k.kk} \qquad (18)$$

Superstructure logical constraint

$$\sum_{kk} y_{kk} V_{kk,step} \leq 1 \qquad (19)$$

$$f_{i,kk}^{W} \leq y_{kk} M \qquad (20)$$

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

$$\sum_i f_{i,kk}^{IN} \leq y_{kk}M \tag{22}$$

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
γ	Stoichiometric coefficient
μ	Ratio of chemical consumption based on reference componant

v	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
$\boldsymbol{react}$	Key reactant, a subset of i
$\boldsymbol{step}$	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

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