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Process of Pretreatment and Hydrolysis of Lignocellulose from Palm Empty Fruit Bunch
for Xylose and Glucose Production



Miss Pitchaya Teerakulkittipong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

FACULTY OF ENGINEERING

Chulalongkorn University

Academic Year 2021

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ไซโลสและกลูโคส



น.ส.พิชญา ธีรกุลกิตติพงศ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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ปีการศึกษา 2564

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

| | |
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| Thesis Title | Process of Pretreatment and Hydrolysis of Lignocellulose from Palm Empty Fruit Bunch for Xylose and Glucose Production |
| By | Miss Pitchaya Teerakulkittipong |
| Field of Study | Chemical Engineering |
| Thesis Advisor | Assistant Professor PONGTORN CHAROENSUPPANIMIT, Ph.D. |

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พินญา ธีรกุลกิตติพงศ์ : กระบวนการปรับสภาพและไฮโดรไลซิสของลิกโนเซลลูโลสจากทะลาย
ปาล์มสำหรับผลิตน้ำตาลไซโลสและกลูโคส. (Process of Pretreatment and Hydrolysis of
Lignocellulose from Palm Empty Fruit Bunch for Xylose and Glucose Production) อ.ที่
ปรึกษาหลัก : ผศ. ดร.พงศ์ธร เจริญศุภนิมิตร

ทะลายปาล์มเปล่าเป็นวัตถุดิบชีวมวลลิกโนเซลลูโลสตัวหนึ่งที่น่าสนใจสำหรับการผลิตน้ำตาล
อย่างไรก็ตามองค์ประกอบลิกนินนั้น ยังจำกัดการเข้าทำปฏิกิริยาไฮโดรไลซิสของสารเคมีกับเฮมิเซลลูโลสและ
เซลลูโลส ซึ่งทั้ง 2 องค์ประกอบนี้ถือเป็นแหล่งของน้ำตาล ดังนั้นในกระบวนการจึงจำเป็นต้องประกอบด้วย
ขั้นตอนการปรับสภาพเพื่อกำจัดลิกนินและไฮโดรไลซิสเพื่อเปลี่ยนเฮมิเซลลูโลสและเซลลูโลสให้เป็นน้ำตาล
ในงานวิจัยนี้มีวัตถุประสงค์เพื่อออกแบบแบบจำลองกระบวนการผลิตน้ำตาลโดยใช้สารเคมีปรับสภาพที่
แตกต่างกัน ได้แก่ เบส (NaOH) และกรด (H_2SO_4) และเปรียบเทียบกระบวนการต่อเนื่องอื่นๆภายหลังการ
ปรับสภาพ นอกจากนี้แล้วยังประเมินค่าทางเศรษฐศาสตร์อีกด้วย โดยโมเดลกระบวนการผลิตน้ำตาล
ออกแบบและจำลองโดยใช้ซอฟต์แวร์ Aspen Plus และใช้ Aspen Economics Analyzer สำหรับการ
วิเคราะห์ค่าทางเศรษฐศาสตร์ จากผลการศึกษพบว่าการใช้สารเคมีปรับสภาพที่แตกต่างกัน ส่งผลให้เกิด
การเปลี่ยนแปลงโครงสร้างของลิกโนเซลลูโลสและกระจายตัวขององค์ประกอบที่ต่างกันด้วย โดยการ
ปรับสภาพโดยใช้เบส สามารถแยกทั้งเฮมิเซลลูโลสและเซลลูโลสออกมาจากลิกนินได้และยังอยู่ในเฟส
ของแข็ง เมื่อเข้าสู่กระบวนการไฮโดรไลซิสแบบ 2 ขั้นตอน จะได้น้ำตาล 2 ชนิดที่เกิดขึ้นแยกกัน ได้แก่ ไซโลสและ
กลูโคส ที่ความเข้มข้น 50.25% และ 76.04% ตามลำดับ และเนื่องด้วยกระบวนการผลิตที่มีความซับซ้อน
มากทำให้ค่าการลงทุนสูง แต่อย่างไรก็ตามยังคงมีกำไรมากกว่า จึงเหมาะกับการลงทุนที่มีความพร้อมและไม่
ต้องการผูกขาดกับผลิตภัณฑ์เพียงชนิดเดียว ส่วนการปรับสภาพโดยใช้กรดนั้น สามารถแยกเฮมิเซลลูโลส
ออกมาได้ดีแต่ไม่สามารถแยกเซลลูโลสออกมาได้ การไฮโดรไลซิสจึงใช้แบบขั้นเดียว และได้น้ำตาลไซโลสซึ่ง
มีความเข้มข้นที่ 50.32% เพียงชนิดเดียว เนื่องด้วยกระบวนการผลิตที่มีความซับซ้อนน้อยกว่าทำให้ค่าการ
ลงทุนต่ำแต่ก็มีกำไรน้อย จึงเหมาะสำหรับการลงทุนที่มีเงินทุนไม่สูงและต้องการไซโลสเพียงชนิดเดียว

สาขาวิชา วิศวกรรมเคมี

ปีการศึกษา 2564

ลายมือชื่อผู้จัดทำ
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Pitchaya Teerakulkittipong : Process of Pretreatment and Hydrolysis of Lignocellulose from Palm Empty Fruit Bunch for Xylose and Glucose Production. Advisor: Asst. Prof. PONGTORN CHAROENSUPPANIMIT, Ph.D.

Oil palm empty fruit bunch is an interesting lignocellulose feedstock for sugar production. However, lignin prohibits chemicals from accessing the hemicellulose and cellulose, which is the source of sugar. Therefore, the overall process requires pretreatment to remove lignin and hydrolysis to convert hemicellulose and cellulose to sugar. In this research, the aim is to design a process model of sugar production using different pretreatment chemicals, including alkaline (NaOH) and acid (H_2SO_4), and compare the other necessary following process. Moreover, capital investment is also estimated. According to the results, different pretreatment chemicals results in a different change of lignocellulose structure and component distribution. In alkaline case, both hemicellulose and cellulose can be separated from lignin. When entering the next process, two-stage hydrolysis is chosen. Xylose and glucose are produced separately with a concentration of 50.25% and 76.04%, respectively. According to the highly complex process, the investment cost is high. However, it appear a higher profit. So, this process is suitable for investments with high capital and high profit margins. Moreover, it can accommodate the risk of xylose price fluctuations. In terms of acid case, hemicellulose is well separated but cellulose can not be isolated. One-stage hydrolysis is used. The produced sugar is xylose, which has a concentration of 50.32%. Because of the less complicated process, investment costs are reduced. Unfortunately, profits are also low. Thus, this process is suitable for investments with low capital and required only xylose products.

Field of Study: Chemical Engineering

Student's Signature

Academic Year: 2021

Advisor's Signature

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Pitchaya Teerakulkittipong

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Chapter 1

Introduction

1.1 Background

Oil-palm is one of the major economic crops in Thailand. The oil-palm plantation has spread to many provinces in the southern area. Moreover, the palm oil industry has developed continuously since 2003. The production of crude palm oil of 700,000 tons/year creates waste comprising of 600,000 tons/year of fiber, 200,000 tons/year of shell palm and 900,000 tons/year of oil palm empty fruit bunch (OPEFB) [1]. Considering the waste generated by this waste, OPEFB is the main waste obtained from the palm-oil industry. Currently, OPEFB is considered as one of the most abundant lignocellulosic feedstocks that is available for the low-efficiency production of energy via direct combustion [2].

Among the lignocellulosic wastes obtained from the oil-palm industry, OPEFB is still not utilized to its full potential (low-efficiency production of energy as mentioned earlier). Typically, OPEFB contains approximately 40-50% of cellulose (or glucan), 25-30% of hemicellulose (or xylan) and 15-20% of lignin. So, the cellulose can be hydrolyzed into hexose and the hemicellulose can be hydrolyzed into pentose [3].

One of the interesting options to increase the value of OPEFB is to convert it into sugar. According to sugar is perceived as a starting material for syntheses of a wide range of value-added chemicals, e.g., xylitol, ethanol, lactic acid, succinic acid and more [4],[5]. So, the conversion of OPEFB into valuable chemicals via the sugar platform merits attention, especially by those involved in the oil-palm industry.

However, lignin prohibits hydrolysis chemicals from accessing the hemicellulose and cellulose, which are the sources of sugar. From these facts, the process for converting OPEFB into valuable chemicals via the sugar platform requires pretreatment to remove lignin first [6].

According to global sugar production, it appears that sugar is produced mainly by sugar canes – about 80% of sugar is produced from this source [7]. Given the problems of climate change and less availability of farmland, sugar production could be directly

affected as a result of a reduced amount of harvested sugar canes. To remedy this, lignocellulosic biomass that contains cellulose, hemicellulose, and lignin could be utilized as an alternative for the sugar production.

Thus, this research is focused on designing a process model of sugar production in which xylose is the main product to be synthesized. The procedure begins with oil palm empty fruit bunches as a starting material. Different pretreatment chemicals, including alkaline (NaOH) and acid (H_2SO_4) are considered to design and compare the other necessary subsequent processes. Process simulation software, namely ASPEN PLUS V11, is utilized for design and simulation. ASPEN ECONOMICS ANALYZER V11 is utilized for analyses of process performances which are to be assessed in terms of economics.

1.2 Objectives of this research

- 1.2.1 To design a process model of sugar production using different pretreatment chemicals.
- 1.2.2 To simulate the pre-hydrolysis and the hydrolysis of lignocellulose from OPEFB
- 1.2.3 To assess the capital process cost of each process
- 1.2.4 To forecast the xylose and glucose capital costs associated with each process.

1.3 Scopes of this research

- 1.3.1 Oil palm empty fruit bunch is a starting raw material for producing xylose and glucose.
- 1.3.2 The produced sugar is used as a starting material in the production of other value-added chemicals.
- 1.3.3 A process design including pretreatment and hydrolysis.
- 1.3.4 Economics are evaluated under a project lifetime and payout period of 10 and 5 years, respectively.

1.4 Schedule plan

| No. | | Activity | Plan | | | | | | | | | | | | | | | | | | | | | | | |
|-----|---|----------|------|---|---|---|----|----|----|---|---|---|---|---|------|---|---|---|----|----|----|---|---|---|---|---|
| | | | 2020 | | | | | | | | | | | | 2021 | | | | | | | | | | | |
| | | | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 |
| 1 | Finding a meaningful topic for the master study | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | Defining a scope and objectives | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 | Compiling literature data | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4 | Developing a process model | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | Executing the process model | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | Analyzing the design results | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | Solve problems of the design model | | | | | | | | | | | | | | | | | | | | | | | | | |
| 8 | Verifying the design results | | | | | | | | | | | | | | | | | | | | | | | | | |
| 9 | Conducting economic analysis | | | | | | | | | | | | | | | | | | | | | | | | | |
| 10 | Comparing economics results | | | | | | | | | | | | | | | | | | | | | | | | | |
| 11 | Summary design and economics results | | | | | | | | | | | | | | | | | | | | | | | | | |

Chapter 2

Theory and literature reviews

2.1 General information of oil-palm empty fruit bunch (OPEFB) component

Oil-palm empty fruit bunch (OPEFB) is a solid waste residue generated from palm oil factories. It has a higher content of lignocellulosic material compared to other types of commodity biomass such as sugarcane bagasse, rice straw, sorghum straw, and corn cobs [6,8].

The constituents of lignocellulosic biomass vary according to types, species, and sources. The main component of lignocellulosic biomass is cellulose, which is abundantly found in plant cell walls, followed by hemicellulose and lignin [9].

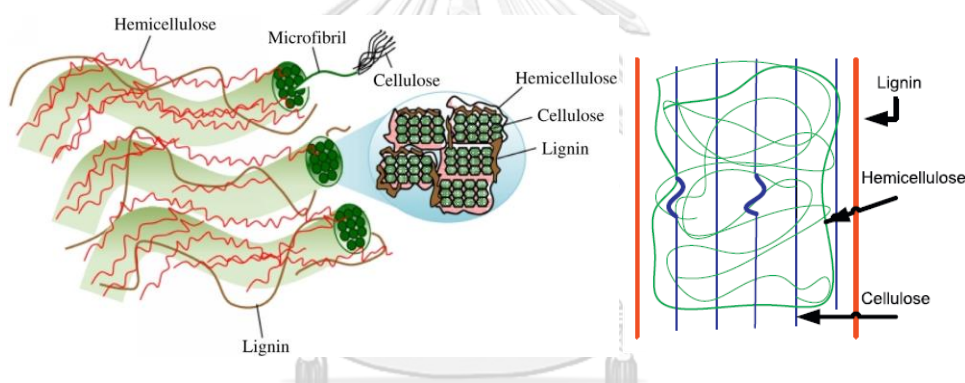


Figure 1. Chemical structure of lignocellulose [9]

2.2 Lignocellulose component

Lignocellulose is a primary building block of a plant cell wall. Plant biomass is mainly composed of 40-50% of cellulose, 25-30% of hemicellulose, and 15-20% of lignin, along with smaller amounts of pectin, protein, extractives (soluble nonstructural materials such as nonstructural sugars, nitrogenous material, chlorophyll, and waxes) and ash [3],[10].

2.2.1 Cellulose

Cellulose is a linear polymer of D-glucopyranose units bounded by β -1-4-glycosidic linkages. Cellulose is repeating units of glucose terminated by a hydroxyl group. These hydroxyl groups (OH) act as functional groups which can interact with other functional groups (e.g. O-, N-, and S-groups) and form hydrogen bonds. Through the hydrogen

bond, cellulose chains are packed closely, providing a highly crystalline structure of microfibrils. This microfibril can be hydrolyzed into glucose either by enzymatic or by chemical methods [8].

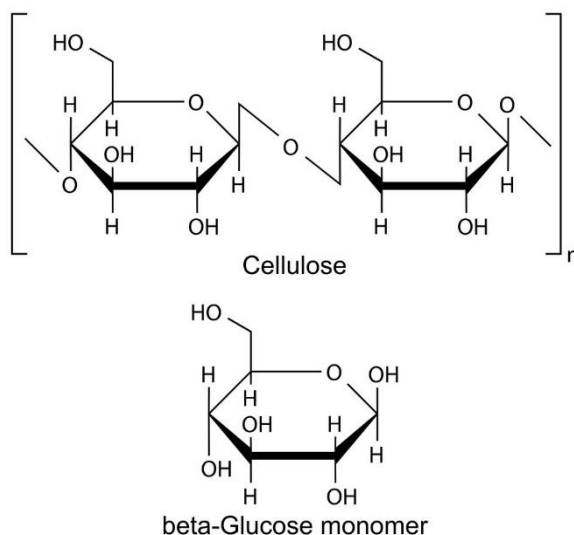


Figure 2. Chemical structure of cellulose and glucose [11]

2.2.2 Hemicellulose

Hemicellulose is a heterogeneous polymer composed of many sugars, such as xylose, arabinose, mannose, and galactose which are C5 and C6 sugars. Its structure is not crystalline. Therefore, it is easier to hydrolyze than cellulose. Hemicelluloses are usually cross-linked to other polysaccharides, proteins or lignin. Xylan is the main component of heterogeneous polysaccharides in hemicellulose and is considered to be the main interface between lignin and other carbohydrates [8,9].

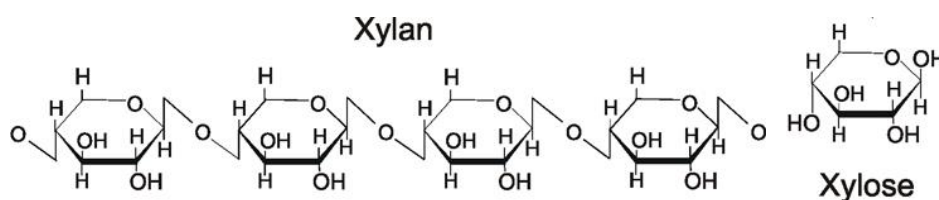


Figure 3. Chemical structure of xylan and xylose [11]

2.2.3 Lignin

Lignin is a cross-linked aromatic, hydrophobic, and complex polymer consisting of three different phenyl-propane precursor monomer units which are very difficult to

biodegrade. Lignin is mostly observed as an integral part of the plant cell wall, embedded in a polymer matrix of cellulose and hemicellulose. Thus, lignin is the most non-biodegradable component of the plant cell wall [8].

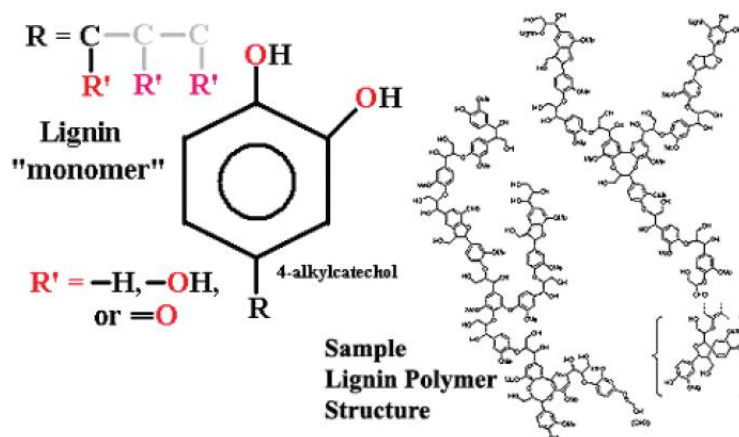


Figure 4. Chemical structure of lignin [8]

2.3 Relevant processes

2.3.1 Pretreatment

Pretreatment is the crucial step in the conversion of energy from lignocelluloses. It is required to open up the plant cell wall and break up the lignocellulose structure, thus making the carbohydrates more accessible to either acid or enzyme in subsequent hydrolysis [6]. Selection of a suitable pretreatment process should consider the compatibility of feedstocks, enzymes and organisms. The process can generally be classified into physical, chemical, physicochemical, or biological methods [3].

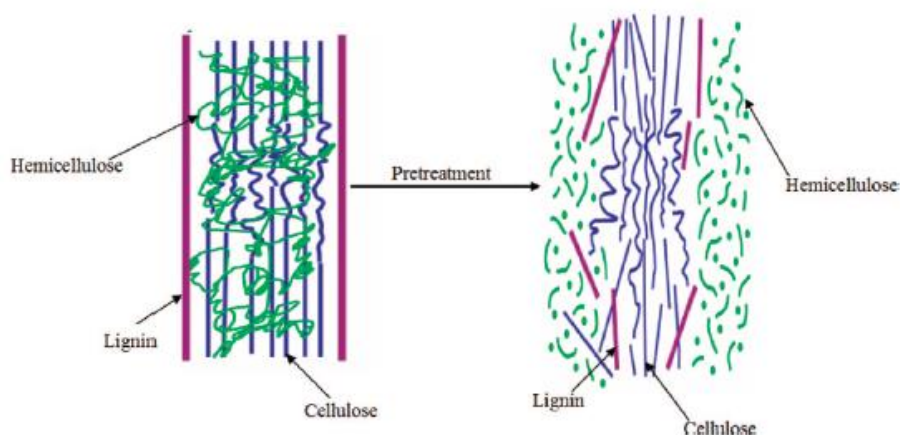


Figure 5. Schematic of the role of pretreatment in the conversion of biomass [10]

- Alkaline pretreatment

A method of Alkaline pretreatment commonly utilizes ammonium, calcium, sodium, and potassium hydroxides as substrates at certain ranges of temperatures and pressures [8]. The main advantage of this method is that lignin is efficiently removed from the biomass. This process eliminates acetyl and uronic acid groups contained in hemicelluloses; as a result, the accessibility of enzyme that degrades hemicellulose increases [8]. Xylan ester linkages on hemicellulose residues are also hydrolyzed. Alkaline pretreatment can also be performed at lower temperatures, pressures, and time ranging from hours to days [8]. NaOH solution is more effective than other alkaline [8]. Moreover, this pretreatment method appears more effective in decreasing the degree of polymerization and crystallinity, increasing the internal surface area of cellulose, and disrupting the lignin structure [8]. Besides NaOH, $\text{Ca}(\text{OH})_2$ (lime) is another widely used alkaline. It also eliminates lignin-carbohydrate ester and acetyl groups which enhances cellulose digestibility. In addition, alkaline can be easier recovered from hydrolysate by a reaction with CO_2 [8].

- Acid pretreatment

Acid pretreatment appears to be a promising method for treating a wide range of lignocellulosic biomass in industrial applications. Under acidic conditions, hemicellulose is more easily degraded to monomeric sugars and by-products than cellulose due to the amorphous structures. Most of the lignin and cellulose components are retained in the acid-insoluble residues. Soluble sugars hydrolyzed by acid during pretreatment can be further degraded to furfural -which is produced from pentoses- and 5-hydroxymethylfurfural (5-HMF) -which is produced from hexoses [12].

Acid pretreatment has been carried out at temperatures of $120 \sim 180^\circ\text{C}$, acid concentrations of 0.2~2% (w/w) and reaction times within 60 min. The most widely used approach is based on sulfuric acid. Nitric acid, hydrochloric acid, phosphoric acid and organic acids have also been shown to be effective [12]. Furthermore, the diluted acid pretreatment methods have been developed in different types of reactors including

percolation plug flow, shrinking-bed, batch, flow-through reactor and countercurrent reactors [8].

The dilute acid pretreatment method is more attractive because of its lower inhibitor formation, such as furfural, hydroxymethylfurfural, phenolic acids, and aldehydes [8]. In addition, diluted acids are less toxic, corrosive, hazardous, and corrosive, as well as more feasible for industrial scale [8].

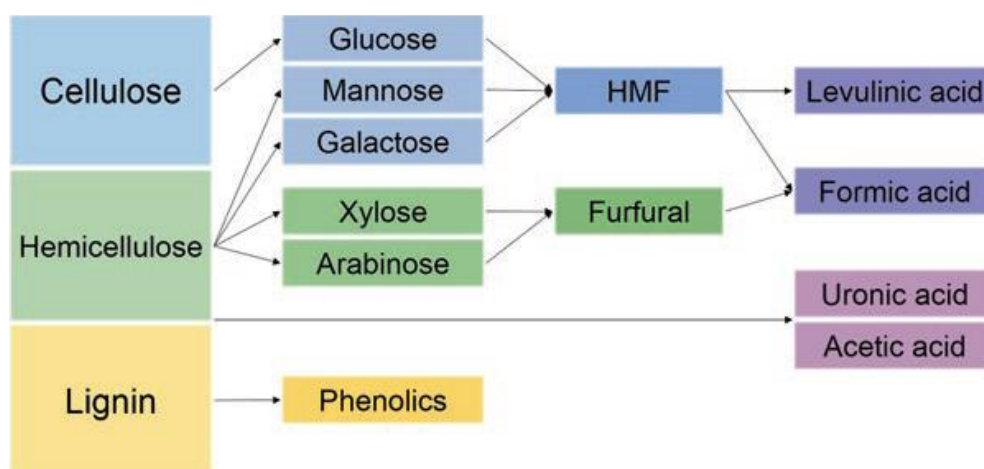


Figure 6. Degradation of lignocellulosic biomass in acidic pretreatment [12].

Table 1. Advantages and disadvantages of different pretreatment methods of lignocellulosic biomass [8,13].

| Pretreatment method | Advantages | Disadvantages |
|---------------------|---|---|
| Alkali | <ul style="list-style-type: none"> Yield is high. Hemicellulose and cellulose are solubilized. lignin is efficiently removed | <ul style="list-style-type: none"> Costs of alkaline catalyst are high. Alteration of lignin structure |
| Acid | <ul style="list-style-type: none"> Yield is high. Hemicellulose is solubilized. | <ul style="list-style-type: none"> Acid recovery is needed. Costs of corrosive resistant equipment are high. Fermentation inhibitors are formed. |

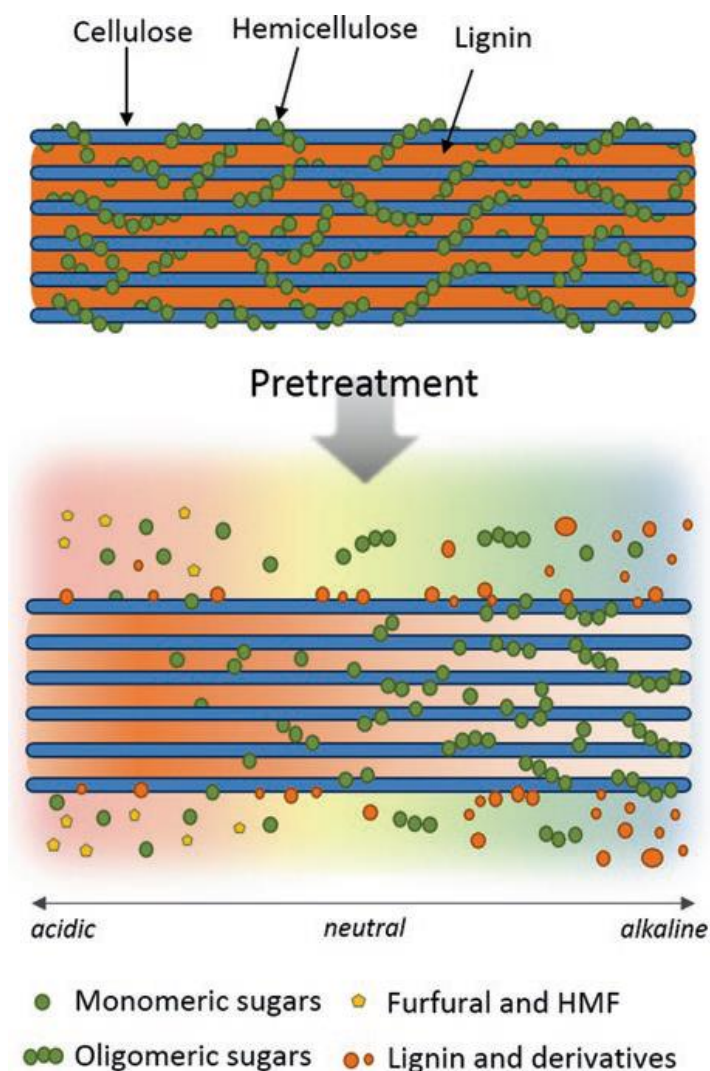


Figure 7. Effects of acid and alkaline pretreatment on solubilization of hemicellulose and lignin in lignocellulose [12].

2.3.2 Acid hydrolysis

Acid hydrolysis (pre-hydrolysis) is used primarily for digesting the hemicellulose. The non-glucose-polymeric carbohydrate (or hemicellulose) contained in lignocellulosic biomass is much more sensitive to acid hydrolysis than the glucose-polymeric carbohydrates [13]. Although hemicellulosic sugars, especially xylose, can be easily obtained using the acid hydrolysis at low temperatures, the hydrolysis is usually performed at high temperatures (between 100 and 160 °C) – the hydrolysis of hemicellulose is accelerated at elevated temperatures owing to a relatively high activation energy in the solid-liquid phase reaction [13]. At high temperatures, xylose

partially released from the hemicellulose can be degraded rapidly and cellulose can be simultaneously hydrolyzed to yield glucose [13]. Acid hydrolysis is effective in processing the hemicellulosic component in a biomass. Moreover, proper selections of operating conditions, e.g., pH, temperature, and reaction time can result in high yields of sugars, primarily xylose from hemicellulose [13]. However, in the hydrolysis, some by-products are generated, such as acetic acid, furfural, phenolic compounds, or lignin degradation products. These are potential inhibitors for a downstream process of microbiological digestion [13].

The main advantages of the acid hydrolysis of biomass include 1) the production of a soluble pentose stream that can be physically separated from the particulate residue and 2) a substantial increase in the rate of the enzymatic hydrolysis of the cellulose [13]. However, this process produces furfural that is toxic to many microorganisms and the acid must be subsequently neutralized [13].

2.3.3 Enzymatic hydrolysis

Enzymatic hydrolysis (Hydrolysis) is a process that can convert cellulose to glucose. An enzyme called cellulase facilitates the cleavage of β -glucosidic bonds in cellulose and produces glucose. This process requires the synergistic action of three core types of enzymes which are endoglucanase (EG), cellobiohydrolase (CBH) and β -glucosidase (BG). EG randomly cleaves internal bonds in the cellulose fiber, creating free chain ends. CBH sequentially cleaves cellobiose units from free chain ends, and BG releases glucose units from cellobiose [15,16].

This process occurs through a complex system of reactions involving several steps. These steps are (1) transfer of enzymes from the bulk aqueous phase to the surface of the cellulose particles, (2) adsorption of the enzymes and formation of enzyme-substrate complexes (ES), (3) hydrolysis of cellulose, (4) transfer of the cellodextrins, glucose and cellobiose, from the surface of the cellulosic particles to the bulk aqueous phase, and (5) hydrolysis of cellodextrins and cellobiose into glucose in the aqueous phase.

Adsorption of enzymes and the formation of enzyme-substrate complexes are considered to be critical steps in the enzymatic hydrolysis of cellulose [16].

Although, cellulose can be hydrolyzed to glucose monomers using chemical catalysts in a quick process. However, it suffers from several limitations such as high-energy requirement, high capital cost, corrosion, durable equipment, high disposal cost, and formation of degraded products [17]. Enzymatic hydrolysis is an alternative to acid hydrolysis that operates at high solids concentration and is essential for the commercial scale of lignocellulosic conversion due to several advantages, including 1) the increased concentrations of obtained sugars and fermentation products and 2) the lower capital and operating costs [15].

2.4 Literature Reviews

2.4.1 Compilation of experimental data for the production of value-added chemicals via the sugar platform

Ying et al. (2014) studied the effects of various pretreatment methods on oil palm empty fruit bunch (EFB) and kenaf core fibers for conversion into sugar for bioethanol production. Un-treat, water, acid (H_2SO_4) and alkaline (NaOH) pretreatment of EFB and kenaf core fibers were carried out at a liquid: solid ratio of 12:1, time 60 min, concentration 2% (v/v) for acid and alkaline, temperature 170°C , 120°C and 120°C , respectively [18]. After that, enzymatic hydrolysis was conducted to consider the effect of pretreatment on the conversion of fibers to sugar. Moreover, the chemical composition is also analyzed [18]. According to the enzymatic hydrolysis results, the untreated EFB and kenaf core fibers were hard to hydrolyze, yielding only 2.6% and 0.4% of reducing sugar (glucose), respectively. In addition, based on the results obtained, by adopting merely water, acid and alkaline pretreatments, the total glucose yields were increased to 34.9%, 34.2% and 27.9% for EFB fiber, while 19.3%, 11.7%, and 12.6% for kenaf core fiber, respectively [18]. The high lignin amount remaining in the fiber caused a decrease in enzymatic saccharification yield and consequently, lowered the total glucose yield [18]. Results of chemical composition analysis indicated the increase in sugar production was highly related to the removal of hemicellulose

and/or lignin in the fibers [18]. It was concluded that without any pretreatment, the natural chemical and physical properties of the EFB and kenaf core fibers limited the conversion of sugar from cellulose by enzymatic hydrolysis [18]. The hydrolysability of the fiber was significantly improved by using simple aqueous pretreatments with water, acid, and alkaline mediums. Furthermore, pretreated EFB fiber exhibited the highest total glucose yield of all the pretreatments [18].

Chong et al (2013) studied the sugar production from OPEFB and the efficiency of sugar conversion obtained from the pre-hydrolysis at different acid concentrations. Dilute-acid pretreatment was performed at various concentrations of 4.0, 6.0 and 8.0% (w/v) of sulfuric acid, with a mass ratio of solid OPEFB to liquid at 1:8 (g/g). The mixture of OPEFB and dilute acid was autoclaved at 120 °C for 15 min. Then, the effluent from the pre-hydrolysis was recovered from solid residue by filtration using Whatman filter paper (pore size 0.45 mm) and neutralized to pH 6.0-7.0 using 5 M sodium hydroxide (NaOH). After that, pentose and hexose contained in the pre-hydrolysis effluent were measured. The experiments revealed that the concentration of the dilute acid used in pretreating and hydrolyzing OPEFB fiber had a strong impact on the sugar production yield and the conversion-to-sugar efficiency. In addition, xylose and glucose concentrations were increased when acid concentration increased from 4% to 6% but both sugar concentrations decreased at 8% of the acid concentration. It was implied that optimal condition for pretreatment was obtained when OPEFB was hydrolyzing at 6% (w/v) sulfuric acid concentration, which gave the highest total sugar of 26.89 g/L and 78.51% of sugar production yield [6]. Furthermore, it was found that pretreatment using dilute acid conducted at high temperatures softened lignin (the structure that encompasses the hemicellulose fiber) facilitating the penetration of acid to hydrolyze the amorphous xylan (hemicellulose fiber) to xylose. In addition, this pretreatment condition was not too severe – the formation of glucose was caused by the hydrolysis of glucan (hemicellulose fiber) whereas cellulose was not disturbed [6]. This led to the attainment of high concentration of xylose in pre-hydrolysis effluent while most of the cellulose remained in the solid. Given that a mixture of sugars are hard to purify (e.g. a mixture of

glucose and xylose), a process that can selectively hydrolyze only hemicellulose is useful to attain a high concentration of xylose [6].

Chavan et al. (2021) studied the effect of different physicochemical parameters and analyzed their effects on enzymatic hydrolysis in the conversion process of lignocellulosic biomass to bioethanol. They also determined the optimum conditions that provided the higher productivity and the reduced operational costs. In the experiments, 200 mg of bamboo was fed to a 30 mL fixed batch reactor. The total of 16 enzymatic hydrolysis experiments: varied cellulase concentrations (5, 10, 15, and 20 % of dry biomass (w/w)), varied temperatures (32, 40, 48, and 56 °C), varied pH of phosphate-citrate buffers (4, 5, 6, 7) and the mixing speeds (0, 60, 120, 180 rpm), were carried out. Experiments were conducted for 48 h. After 48 h of reaction time, the solid and liquid portions in the slurry were separated by a filtration. Liquid hydrolysates were further analyzed for a determination of glucose. The results showed that the enzyme/substrate ratio and the solution pH were proved to be the most significant factors whereas the temperature, the mixing speed and the particle size showed lower influence. The results also showed that maximum product yield could be obtained at 5 of the pH value, 48 °C, enzyme-substrate ratio of 20%, zero mixing speed and the particle size below 60 μm [14]. By studying the effect of each parameter affecting enzymatic hydrolysis, it provides a better understanding of the process that can be applied to this designed process – i.e., how to process the OPEFB appropriately to obtain desired products.

Gonzales et al. (2019) used Response Surface Methodology (RSM) to determine the optimum conditions of dilute acid and enzymatic hydrolysis for the hydrogen production via dark fermentation from the empty fruit bunch of oil-palm. In dilute acid hydrolysis experiments, factors including the temperature, the H_2SO_4 concentration, and the hydrolysis time were considered. Central values for each factor were 100 °C, 5% H_2SO_4 , and 45 min of reaction time with intervals of: ± 20 , ± 1 , ± 15 respectively [19]. EFB was added into the hydrolysis vessel at a concentration of 10 g/L. Reaction was allowed to occur in an autoclave at a pressure of 0.9 MPa. After determining the optimal conditions of the dilute acid hydrolysis, the EFB residue was sent to the enzymatic hydrolysis. In

this step, temperature, pH, and enzymatic loading were considered. Central values for each factor were 45 °C, 5 pH, and 0.75 mg enzyme/mL with intervals of: ± 15 , ± 2 , ± 0.25 respectively [19]. The RSM was used to design experimental procedures, generate models, evaluate the significance of independent variables, and optimize a response influenced by several variables. Moreover, the RSM could determine the optimal process conditions and identify the limit of a response. After running the RSM, the results showed that the optimum conditions for dilute acid hydrolysis were found at 120 °C, 6 vol% of H_2SO_4 and 60 min of reaction time. Enzymatic hydrolysis optimal conditions were found at 45 °C, 5.0 of the pH value, and 1.17 mg enzyme/mL [19]. From this research, it provides steps involved in conversion of lignocellulose into monosaccharides. Specifically, the results provided in this work revealed the products that occurred in each step allowing a proper design of removal processes.

2.4.2 Compilation of modeling and simulation of lignocellulosic biomass

Arenas et al. (2010) used a process simulator (Aspen Plus) to improve the process efficiency (high conversion and low reaction times) of the acid pretreatment (pre-hydrolysis) of corn stover in a continuous process of ethanol production. In this research, the conversion process of lignocellulosic biomass to ethanol had three main sections which consisted of the pretreatment (pre-hydrolysis), the simultaneous enzymatic saccharification and fermentation, and the purification of ethanol [20]. For the pre-hydrolysis process, the continuous flow reactor operated at high temperature with feeds contained lignocellulosic biomass and dilute sulfuric acid was simulated. Most of the hemicellulose portion was hydrolyzed to soluble sugars (primarily xylose, mannose, arabinose, and galactose). Glucan in the hemicellulose and a trace portion of the cellulose were converted to glucose. Degraded products of pentose and hexose (primarily furfural) were also formed [20]. According to a model, the reactor was simulated based on a design bases of 1.1 % of the acid concentration, 2 minutes of the residence time, 190 °C and 42 wt% of the biomass concentration. Crucial operating parameters were varied to identify the best set of parameters leading to the highest efficiency. The results showed that optimal conditions to achieve the highest conversion

at the residence time of 2 minutes were 160 °C, the dilute concentration of sulfuric acid of 4 % w/w and the mass fraction of biomass in the feed stream of 0.4 [20]. The concept of converting lignocellulose into monosaccharides and their reactions are keys of the pre-hydrolysis. Thus, the information from this section is useful for construction of the simulated model.

NREL [21] has modeled the conversion process of biomass to ethanol via the sugar platform and estimated the economics of their processes. Moreover, their work can be used to predict the cost of producing ethanol if the plant were to be built in the next few years. To construct model, ASPEN modeling software were applied. In this process, corn stover were used as feedstock for a production of ethanol. The process includes pre-hydrolysis, simultaneous saccharification and co-fermentation, and cellulase enzyme production. In addition, all ancillary areas – feedstock handling and storage, product purification, product storage, wastewater treatment, lignin combustion, and utilities - were included. From the results, the minimum ethanol selling price and total investment are based on the minimum number of varied values – stover cost, value of excess electricity, enzyme price, reactor purchase price, project contingency. The process performance can be improved by improving affected parameters - water balance, fermentation pH control, air emissions, greenhouse gas emissions, lignin gasification and power generation, Physical properties of corn stover [21]. This sensitivity analyses, e.g., the conversion of lignocellulose from a corn stover process has been shown useful which should be implemented with other processes of biomass conversions. Plus, it can be used as a guideline of how to produce other value-added chemicals through the sugar platform.

As seen from the literature, the utilization of two-consecutive processes, pretreatment and hydrolysis, is beneficial for the conversion of lignocellulose into monosaccharides. Without these two-consecutive processes, the synthesizing of sugars is difficult and requires a more complex and expensive process. Implementation of these pretreatment and hydrolysis processes into a simulated process offers the advantages of each pretreatment method for changing the structure of lignocellulose -

which provides different product phases- followed by the proper pathway for handling the products after pretreatment -which influences the design of hydrolysis processes.

Yet, the synthesis of value-added chemicals via the sugar platform is currently undertaken only on a lab scale. To justify whether the production can be upscaled to a feasibly commercialized level, a process simulation is required. However, the process simulation describing the production of value-added chemicals via the sugar platform was extremely limited in the literature, especially for the process that uses OPEFB as a feedstock. This leads to the main focus of this work, that is to design a process simulation capable of describing the proper process path of pretreatment and hydrolysis with reasonable accuracy. Moreover, it also evaluates the project's investment cost.



Chapter 3

Methodology

This chapter provides steps involved in creating a process model describing the conversion of lignocellulose from oil-palm empty fruit bunch (OPEFB) into monosaccharides and identifies key parameters influencing the process feasibility. In this research, there are 7 steps consisting of 3.1) defining the problem, 3.2) collecting necessary data for creating the process model, 3.3) calculating the required feed amounts from the experimental data, 3.4) creating the process flowsheet, 3.5) executing the flowsheet and validating the process results, 3.6) conducting the economic analysis and 3.7) forecasting sugar capital cost

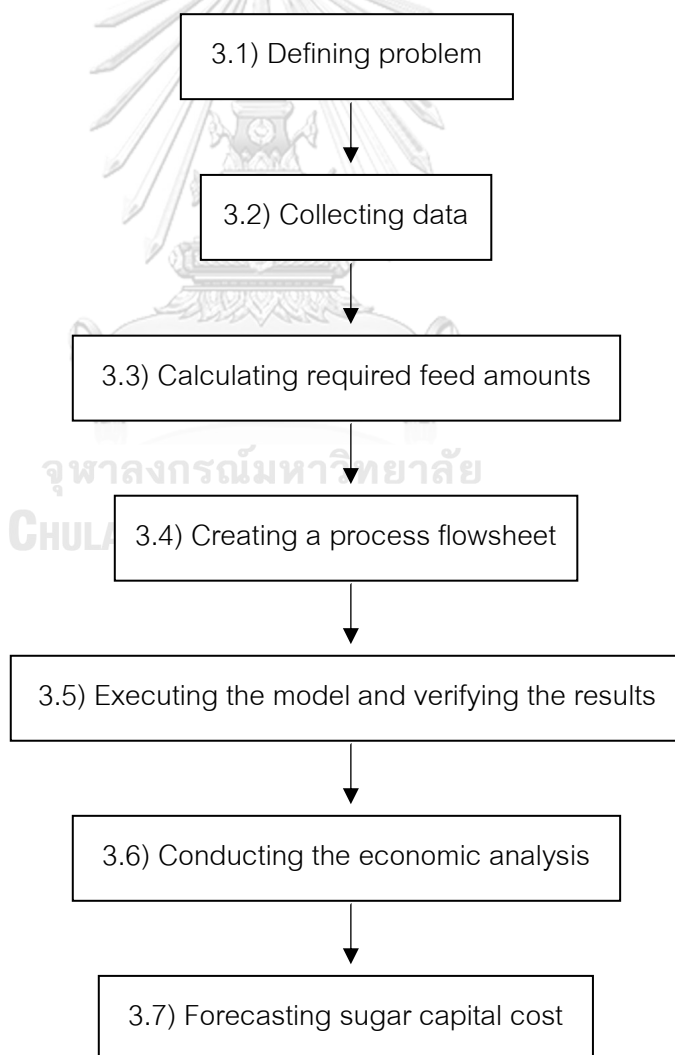


Figure 8. Process methodology

3.1 Defining the problem

To produce value-added chemicals, the lignocellulosic biomass from OPEFB, which is an abundant waste obtained from an oil-palm factory in Thailand, is utilized. To be consistent with our objective, the selected value-added chemical is sugar, especially xylose. Successful development of this process should reduce oil palm waste. Furthermore, sugar can be a starting material for the production of other valuable chemicals.

3.2 Collecting necessary data for creating the process flowsheet

3.2.1 Feedstock

Feedstock for this process is oil-palm empty fruit bunch, which is a lignocellulosic material. The major components and their compositions are given in Table 2.

Table 2. Main components of OPEFB(dry basis of OPEFB biomass) [6]

| Main fraction | Mass Composition (%) |
|-------------------------|----------------------|
| Cellulose | 38.09 |
| Hemicellulose | 29.93 |
| Lignin (acid insoluble) | 15.96 |
| Ash | 0.54 |
| Extractives | 15.48 |

*Assuming that biomass has the same structure of cellulose hemicellulose and lignin.

3.2.2 Pretreatment

In this process, the pretreatment is performed in an isothermal reactor at 120 °C and 1 atm for 60 minutes. The mass ratio of solid OPEFB to liquid is maintained at 1:12. Different pretreatment chemicals, sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH), are considered at a concentration of 1.1 % (v/v) for both. The reactions are given below [18].

Table 3. Operating conditions for pretreatment [18]

| Condition | Value |
|-------------|--------|
| Temperature | 120 °C |
| Pressure | 1 atm |

| | |
|--|------------|
| NaOH Concentration | 1.1 %(v/v) |
| H ₂ SO ₄ Concentration | 1.1 %(v/v) |
| Resident time | 60 min |
| Liquid: Solid | 12: 1 |

- Alkaline pretreatment case

- 1) Hemicellulose (s) + H₂O → Hemicellulose (l) conversion 0.49
- 2) Cellulose (s) + H₂O → Cellulose (l) conversion 0.38
- 3) Lignin (s) + H₂O → Lignin (l) conversion 0.67

* Desirable phase is solid

- Acid pretreatment case

- 1) Hemicellulose (s) + H₂O → Hemicellulose (l) conversion 0.95
- 2) Cellulose (s) + H₂O → Cellulose (l) conversion 0.24
- 3) Lignin (s) + H₂O → Lignin (l) conversion 0.00

* Desirable phase is liquid

3.2.3 Hydrolysis

In this research, hydrolysis is divided into 2 sections, consisting of pre-hydrolysis and hydrolysis.

Pre-hydrolysis is primarily used for digesting hemicellulose into xylose. The non-glucose-polymeric carbohydrate (or hemicellulose) contained in lignocellulosic biomass is much more sensitive to acid hydrolysis than the glucose-polymeric carbohydrates [13]. So, acid hydrolysis is selected for both cases.

- Alkaline pretreatment case

The isothermal reactor is operated at 190 °C and 12 atm. The mixtures account for 30 %vol of the solids in the reactor. Sulfuric acid is used as a catalyst for the pre-hydrolysis, whose concentration is maintained at 1.1 %(w/w). The reactions are defined below [21].

Table 4. Operating conditions for pre-hydrolysis for alkaline pretreatment case[21]

| Operating condition | Value |
|---------------------|--------------------------------|
| Temperature | 190 °C |
| Pressure | 12 atm |
| Acid | H ₂ SO ₄ |
| Acid concentration | 1.1 %(w/w) |

- 1) Hemicellulose + H₂O → Xylose conversion 0.900
- 2) Hemicellulose → Furfural + 2 H₂O conversion 0.500
- 3) Hemicellulose + H₂O → Xylose oligomer conversion 0.025
- 4) *Cellulose + H₂O → Glucose conversion 0.070
- 5) *Cellulose + H₂O → Glucose oligomer conversion 0.014

*Cellulose side reaction

- Acid pretreatment case

The acid pre-hydrolysis is operated at 140 °C and 1 atm in the isothermal reactor.

The reactions are given below [13].

Table 5. Operating conditions for pre-hydrolysis for acid pretreatment case [13].

| Operating condition | Value |
|---------------------|--------------------------------|
| Temperature | 140 °C |
| Pressure | 1 atm |
| Acid | H ₂ SO ₄ |
| Acid concentration | 0.1 %(w/w) |

- 1) Hemicellulose + H₂O → Xylose conversion 0.734
- 2) Hemicellulose → Furfural + 2 H₂O conversion 0.079
- 3) Hemicellulose + H₂O → Xylose oligomer conversion 0.000

* The conversion of hemicellulose to xylose oligomer is assumed to be 0 based on a small portion of xylose oligomer.

Hydrolysis is a following process that can convert cellulose to glucose. Cellulose can be hydrolyzed to glucose monomers using acid chemical catalysts or an enzyme, called cellulase[15,16].

- Alkaline pretreatment case

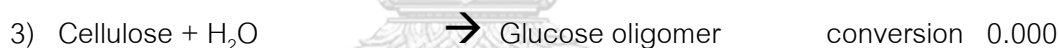
In the alkaline case, enzymatic hydrolysis is selected. An isothermal reactor operated at a pressure of 1 atm and a temperature of 50 °C [22]. A cellulase enzyme whose activity is 13,000 U/ml is introduced to the reactor with a theoretical ratio [22]. The reactions are provided below.

Table 6. Operating conditions for hydrolysis for alkaline pretreatment case [22].

| Operating condition | Value |
|---------------------|-----------|
| Temperature | 50 °C |
| Pressure | 1 atm |
| Enzyme | cellulase |



In the acid case, the hydrolysis occurs simultaneously with the pre-hydrolysis. The condition is the same as the alkaline case. But the reactions are given below [13].



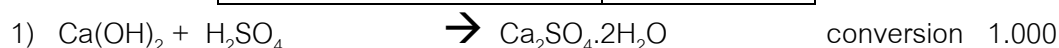
* The conversion of cellulose to glucose oligomer is assumed to be 0 based on a small portion of glucose oligomer.

3.2.4 Neutralization

Neutralization is a processing unit for removing the acid. Calcium hydroxide (Ca(OH)₂) is used as a base for the neutralization which operates in an isothermal reactor at 50 °C [21]. The operating conditions and reaction are given below. Table 7.

Operating conditions for Neutralization [21]

| Operating condition | Value |
|---------------------|---------------------|
| Temperature | 50 °C |
| Pressure | 1 atm |
| Chemicals | Ca(OH) ₂ |



3.3 Calculating required feed amounts

The data from Section 3.2 can be used to calculate the input of each feed stream. Assuming a feed flowrate of dry OPEFB of 3000 kg/hr, other feed streams can also be calculated. The calculated data for feed streams is tabulated in Table 10.

Table 8. Calculated flowrates of feed stream

| Stream | Description | Mass flowrate (kg/hr) | |
|--------------------------|--|-----------------------|-----------|
| | | Alkaline | Acid |
| LIGNO-I | Dry OPEFB feedstock (Flowrate is assumed) | 3,000.00 | 3,000.00 |
| PT-WATER | Water in pretreatment (Condition: solid: liquid ratio is 1:12) | 36,000.00 | 36,000.00 |
| ALK-IN | NaOH added to pretreatment (Condition: concentration 1.1%(v/v)) | 76.67 | - |
| ACID-IN | H ₂ SO ₄ added to pretreatment (Condition: concentration 1.1%(v/v)) | - | 61.06 |
| PH-WATER | Water added to pre-hydrolysis (Condition: 30% solid in reactor) | 2,716.93 | - |
| PH-ACID | H ₂ SO ₄ catalyst added to pre-hydrolysis (Condition: conc.1.1 and 0.1 %w/w respectively) | 50.70 | 109.62 |
| LIME _{alkaline} | CaOH ₂ for neutralize residual H ₂ SO ₄ from pre-hydrolysis (Condition: 1:1 mol) | 32.93 | - |
| LIME _{acid} | CaOH ₂ for neutralize residual H ₂ SO ₄ from pretreatment (Condition: 1:1 mol) | - | 46.89 |
| LIME2 _{acid} | CaOH ₂ for neutralize residual H ₂ SO ₄ from hydrolysis (Condition: 1:1 mol) | - | 81.15 |
| ENZ | Cellulase enzyme added to hydrolysis | 0.07 | - |
| HL-WATER | Water added to hydrolysis for hydrolyzing of cellulose (Condition: 1:1 mol) | 66.66 | - |

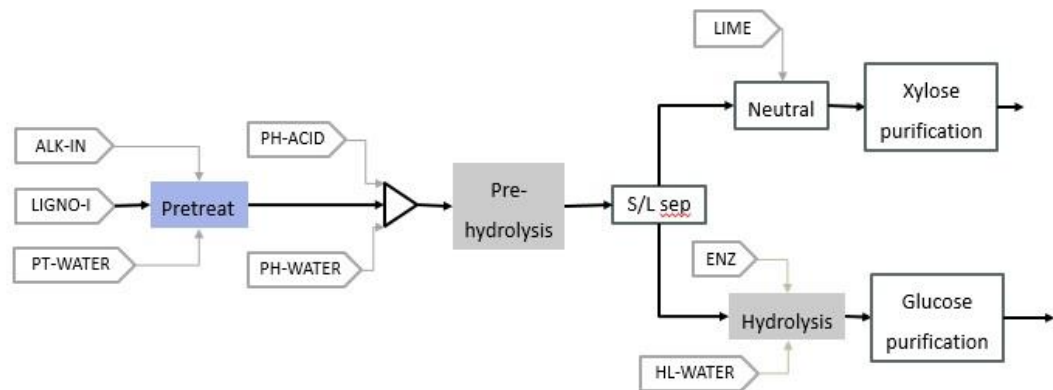


Figure 9. block flow diagram of feed stream in alkaline pretreatment case

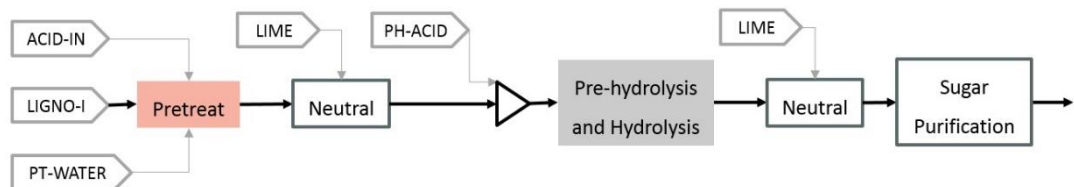


Figure 10. block flow diagram of feed stream in acid pretreatment case

3.4 Creating process flowsheet

The created flowsheet contains 2 main sections, including pre-hydrolysis and hydrolysis. The data for the flowsheet construction are taken from “Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Pre-hydrolysis and Enzymatic Hydrolysis for Corn Stover” [21]. Other sections that are suitable for increasing concentrations of products are also constructed. The flow diagram for converting OPEFB to monosaccharides are depicted in Figure 9 and 10.

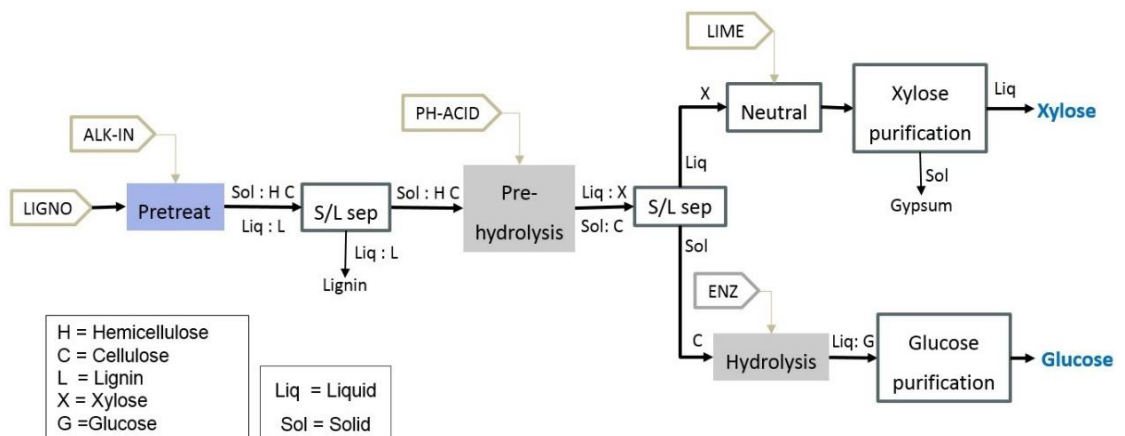


Figure 11. Process block flow diagram of alkaline pretreatment case

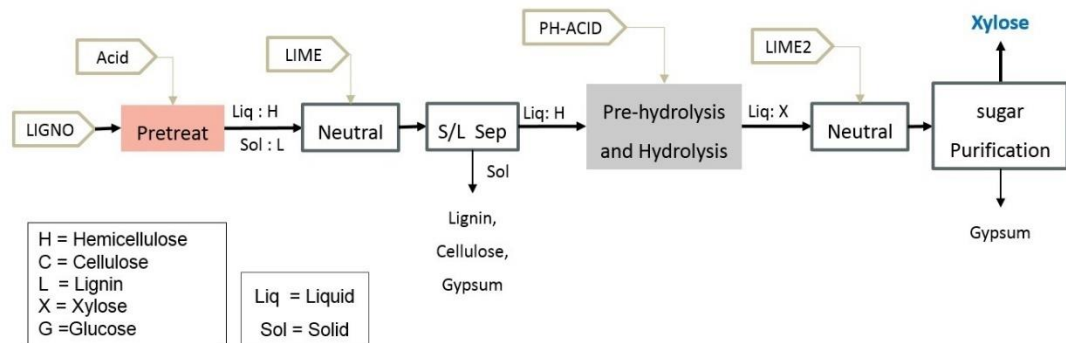


Figure 12. Process block flow diagram of acid pretreatment case

3.5 Executing the process flowsheet and verifying the obtained results

After creating the process flowsheet based on the information obtained from the previous step, the flowsheet is executed, and the results will be verified by checking the simulation results with experimental data. If the executed results are not consistent with the experimental data, the simulated model will be corrected and redone the execution.

3.6 Conducting the economic analysis

The model obtained from the previous step is used as a model for capital cost estimation. Then, the economic performance of the process is evaluated using the Aspen Economic Analyzer. The parameters used in the assessment of economic performance include the profitability index (PI), internal rate of return (IRR), and net present value (NPV).

- Profitability Index (PI)

The PI value indicates whether this project is worth investing or not. PI can be calculated by the following equation.

$$\text{Profitability Index(PI)} = \frac{\text{Present value of future cash flows}}{\text{Initial investment}} \quad (\text{Eq. 1})$$

- If PI is greater than 1, the project should be accepted.
- If PI is less than 1, the project should be rejected [23].

- Internal Rate of Return (IRR)

Internal Rate of Return (IRR) is a financial indicator used for making a comparison with the lowest return such as interest gained from making a bank deposit [23].

- Net present value (NPV)

Net present value (NPV) is the difference between the present value of cash inflows and the present value of cash outflows over a period of time. NPV is used in capital budgeting and investment planning to analyze the profitability of a projected investment [24].

These three parameters are calculated based on a 5-year payout period. Furthermore, the price index has also been updated. The adjustments are shown in the table below [25].

Table 9. The adjustments of construction materials price index and tax rate

| Indexing | Default | Current |
|----------|---------|---------|
| Equip | 100 | 119 |
| Piping | 100 | 119 |
| Steel | 100 | 119 |
| Civil | 100 | 99.2 |
| Tax rate | 40 | 25 |

3.7 Forecasting sugar capital cost

Following the determination of total expenses, the total expenses will be a project capital cost for calculating the capital cost of sugar per kilogram unit.

Chapter 4

Results and Discussion

4.1 Alkaline pretreatment case

4.1.1 Simulation

● Pretreatment

Process flow diagram

OPEFB (LIGNO-I) and water (PT-WATER) with a mass ratio of solid OPEFB to liquid at 1: 12 were heated to 120 ° C. Then, mixtures (LIGNO-O) were fed to a pretreatment reactor (PRET) and performed at a concentration of 1.1%(v/v) of sulfuric acid, 120 °C and 1 atm. After that, the pretreated OPEFB (PT-LIGNO) was recovered from liquid (LIQ-F1) by centrifuge - 95% solid recovery and 20% moisture. A solid stream (SOL-F1) is a desirable phase flow to the next step.

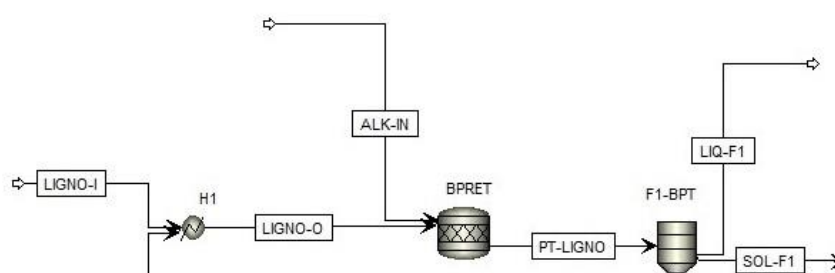


Figure 13. Process flow diagram of pretreatment

Process results

Table 10. Results of pretreatment (1)

| Stream Name | LIGNO-I | LIGNO-O | PT-WATER | ALK-IN |
|--------------|----------|-----------|-----------|--------|
| From | - | H1 | - | - |
| To | H1 | BPRET | H1 | BPRET |
| T (°C) | 25 | 120 | 25 | 120 |
| P (atm) | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 3,000.00 | 39,000.00 | 36,000.00 | 76.67 |
| Component | | | | |
| Ash | 480.60 | 480.60 | 0.00 | 0.00 |
| Xylose oli. | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose oli. | 0.00 | 0.00 | 0.00 | 0.00 |

| Stream Name | LIGNO-I | LIGNO-O | PT-WATER | ALK-IN |
|--------------------------------|----------|-----------|-----------|--------|
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 | 0.00 |
| Cellulose | 1,142.70 | 1,142.70 | 0.00 | 0.00 |
| Enzyme | 0.00 | 0.00 | 0.00 | 0.00 |
| Furfural | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose | 0.00 | 0.00 | 0.00 | 0.00 |
| Gypsum | 0.00 | 0.00 | 0.00 | 0.00 |
| H ₂ O | 0.00 | 36,000.00 | 36,000.00 | 0.00 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 | 0.00 |
| HMF | 0.00 | 0.00 | 0.00 | 0.00 |
| LIGNIN | 478.80 | 478.80 | 0.00 | 0.00 |
| NaOH | 0.00 | 0.00 | 0.00 | 76.67 |
| Xylan | 897.90 | 897.90 | 0.00 | 0.00 |
| Xylose | 0.00 | 0.00 | 0.00 | 0.00 |

Table 11. Results of pretreatment (2)

| Stream Name | PT-LIGNO | SOL-F1 | LIQ-F1 |
|--------------------------------|-----------|----------|-----------|
| From | BPRET | F1-BPT | F1-BPT |
| To | F1-BPT | C0 | - |
| T (°C) | 120 | 120 | 100 |
| P (atm) | 1 | 1 | 1 |
| Flow (kg/hr) | 39,076.67 | 1,986.50 | 37,090.17 |
| Component | | | |
| Ash | 480.60 | 456.57 | 24.03 |
| Xylose oli. | 0.00 | 0.00 | 0.00 |
| Glucose oli. | 0.00 | 0.00 | 0.00 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 |
| Cellulose | 1,142.70 | 779.61 | 363.09 |
| Enzyme | 0.00 | 0.00 | 0.00 |
| Furfural | 0.00 | 0.00 | 0.00 |
| Glucose | 0.00 | 0.00 | 0.00 |
| Gypsum | 0.00 | 0.00 | 0.00 |
| H ₂ O | 36,000.00 | 72.00 | 35,928.00 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 |
| HMF | 0.00 | 0.00 | 0.00 |
| LIGNIN | 478.80 | 174.30 | 304.50 |
| NaOH | 76.67 | 0.00 | 76.67 |
| Xylan | 897.90 | 504.03 | 393.87 |
| Xylose | 0.00 | 0.00 | 0.00 |

Pretreatment (BPRET) is a process that alters the structure of a substance. As a result, lignin is eliminated to allow various chemicals to be able to react with hemicellulose and cellulose. Lignin exists in a liquid phase, whereas cellulose and hemicellulose exist in a solid phase. The next step, F1-BPT is responsible for separating lignin (liquid) from hemicellulose and cellulose (solid). So, the lignin and acid dissolved in the liquid phase (LIQ-F1) can be separated from the pretreated OPEFB (SOL-F1).

*Assuming that the extractives are un-reacting components, the extractive composition was included in the ash.

- Pre-hydrolysis

Process flow diagram

the solid portion (SOL-F1) from previous section was cool to 90 °C. After that, the cooled stream was diluted with water (PH-WATER) and sulfuric acid (PH-ACID) respectively. Then, mixtures (PD-MA) were pumped with screw pump (P1) from 1 atm to 12 atm and heated (H2) from 38 °C to 190 °C to reach pre-hydrolysis conditions.

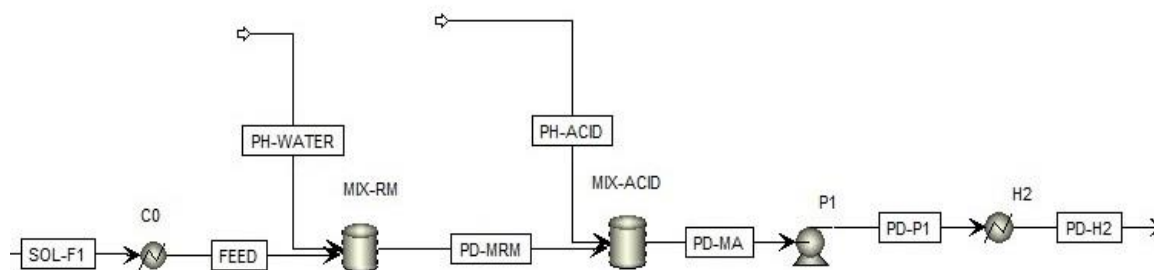


Figure 14. Process flow diagram of Feed preparation for pre-hydrolysis

The prepared feed (PD-H2) was hydrolyzed in an isothermal reactor (PREH) at 190 °C and 12 atm. After pre-hydrolysis, the product (PD-PH) flowed through a valve (V1) to reduce the pressure from 12 atm to 1 atm. Then, a flash (FLS1) at 104 °C was required to vaporize a large amount of water and much of the furfural. Following flash, the slurry product (L-FLS1) was cooled to 65 °C and fed to a centrifuge (F2-XYL) -95%

solid recovery and 5% moisture- to separate between liquid (L-FTX) and solid (S-FTX).

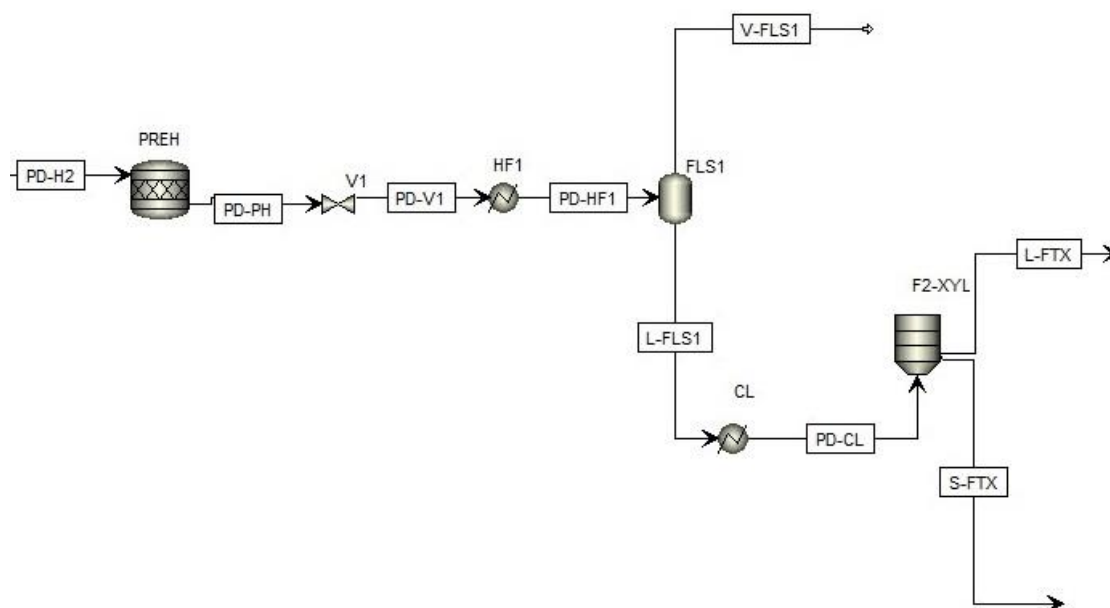


Figure 15. Process flow diagram of pre-hydrolysis

Process results

Table 12. Results of feed preparation for pre-hydrolysis (1)

| Stream Name | FEED | PH-WATER | PD-MRM | PH-ACID |
|--------------------------------|----------|----------|----------|----------|
| From | C0 | - | MIX-RM | - |
| To | MIX-RM | MIX-RM | MIX-ACID | MIX-ACID |
| T (°C) | 90 | 25 | 37 | 25 |
| P (atm) | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 1,986.50 | 2,716.93 | 4,703.44 | 51.74 |
| Component | | | | |
| Ash | 456.57 | 0.00 | 456.57 | 0.00 |
| Xylose oli. | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose oli. | 0.00 | 0.00 | 0.00 | 0.00 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 | 0.00 |
| Cellulose | 779.61 | 0.00 | 779.61 | 0.00 |
| Enzyme | 0.00 | 0.00 | 0.00 | 0.00 |
| Furfural | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose | 0.00 | 0.00 | 0.00 | 0.00 |
| Gypsum | 0.00 | 0.00 | 0.00 | 0.00 |
| H ₂ O | 72.00 | 2,716.93 | 2,788.93 | 1.03 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 | 50.71 |
| HMF | 0.00 | 0.00 | 0.00 | 0.00 |
| LIGNIN | 174.30 | 0.00 | 174.30 | 0.00 |
| NaOH | 0.00 | 0.00 | 0.00 | 0.00 |

| Stream Name | FEED | PH-WATER | PD-MRM | PH-ACID |
|-------------|--------|----------|--------|---------|
| Xylan | 504.03 | 0.00 | 504.03 | 0.00 |
| Xylose | 0.00 | 0.00 | 0.00 | 0.00 |

Table 13. Results of feed preparation for pre-hydrolysis (2)

| Stream Name | PD-MA | PD-P1 | PD-H2 |
|--------------------------------|----------|----------|----------|
| From | MIX-ACID | P1 | H2 |
| To | P1 | H2 | PREH |
| T (°C) | 37 | 38 | 190 |
| P (atm) | 1 | 12 | 12 |
| Flow (kg/hr) | 4,755.18 | 4,755.18 | 4,755.18 |
| Component | | | |
| Ash | 456.57 | 456.57 | 456.57 |
| Xylose oli. | 0.00 | 0.00 | 0.00 |
| Glucose oli. | 0.00 | 0.00 | 0.00 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 |
| Cellulose | 779.61 | 779.61 | 779.61 |
| Enzyme | 0.00 | 0.00 | 0.00 |
| Furfural | 0.00 | 0.00 | 0.00 |
| Glucose | 0.00 | 0.00 | 0.00 |
| Gypsum | 0.00 | 0.00 | 0.00 |
| H ₂ O | 2,789.97 | 2,789.97 | 2,789.97 |
| H ₂ SO ₄ | 50.71 | 50.71 | 50.71 |
| HMF | 0.00 | 0.00 | 0.00 |
| LIGNIN | 174.30 | 174.30 | 174.30 |
| NaOH | 0.00 | 0.00 | 0.00 |
| Xylan | 504.03 | 504.03 | 504.03 |
| Xylose | 0.00 | 0.00 | 0.00 |

After adding water (PH-WATER) and acid (PH-ACID), the total composition of the mixtures in PD-MA is the sum of the compositions in each stream according to the mass balance. When passing through the pump and the heater, the compositions remain the same, but the pressure and temperature are changed.

Table 14. Results of pre-hydrolysis (1)

| Stream Name | PD-PH | PD-V1 | PD-HF1 | L-FLS1 | V-FLS1 |
|-------------|-------|-------|--------|--------|--------|
| From | PREH | V1 | HF1 | FLS1 | FLS1 |
| To | V1 | HF1 | FLS1 | CL | - |

| Stream Name | PD-PH | PD-V1 | PD-HF1 | L-FLS1 | V-FLS1 |
|--------------------------------|----------|----------|----------|----------|----------|
| T (°C) | 190 | 101 | 104 | 104 | 104 |
| P (atm) | 12 | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 4,755.18 | 4,755.18 | 4,755.18 | 2,509.68 | 2,245.50 |
| Component | | | | | |
| Ash | 456.57 | 456.57 | 456.57 | 456.57 | 0.00 |
| Xylose oli. | 12.36 | 12.36 | 12.36 | 12.36 | 0.00 |
| Glucose oli. | 10.47 | 10.47 | 10.47 | 10.47 | 0.00 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cellulose | 723.07 | 723.07 | 723.07 | 723.07 | 0.00 |
| Enzyme | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Furfural | 15.82 | 15.82 | 15.82 | 1.69 | 14.13 |
| Glucose | 52.35 | 52.35 | 52.35 | 52.35 | 0.00 |
| Gypsum | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| H ₂ O | 2,734.75 | 2,734.75 | 2,734.75 | 503.40 | 2,231.35 |
| H ₂ SO ₄ | 50.71 | 50.71 | 50.71 | 50.68 | 0.02 |
| HMF | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| LIGNIN | 174.30 | 174.30 | 174.30 | 174.30 | 0.00 |
| NaOH | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Xylan | 79.87 | 79.87 | 79.87 | 79.87 | 0.00 |
| Xylose | 444.92 | 444.92 | 444.92 | 444.92 | 0.00 |

Table 15. Results of pre-hydrolysis (2)

| Stream Name | PD-CL | L-FTX | S-FTX |
|--------------------------------|----------|----------|----------|
| From | CL | F2-XYL | F2-XYL |
| To | F2-XYL | NEU | C1 |
| T (°C) | 65 | 65 | 65 |
| P (atm) | 1 | 1 | 1 |
| Flow (kg/hr) | 2,509.68 | 1,158.73 | 1,350.95 |
| Component | | | |
| Ash | 456.57 | 22.83 | 433.74 |
| Xylose oli. | 12.36 | 10.63 | 1.73 |
| Glucose oli. | 10.47 | 9.00 | 1.47 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 |
| Cellulose | 723.07 | 122.46 | 600.61 |
| Enzyme | 0.00 | 0.00 | 0.00 |
| Furfural | 1.69 | 1.46 | 0.24 |
| Glucose | 52.35 | 45.02 | 7.33 |
| Gypsum | 0.00 | 0.00 | 0.00 |
| H ₂ O | 503.40 | 432.92 | 70.48 |
| H ₂ SO ₄ | 50.68 | 43.59 | 7.10 |

| Stream Name | PD-CL | L-FTX | S-FTX |
|-------------|--------|--------|--------|
| HMF | 0.00 | 0.00 | 0.00 |
| LIGNIN | 174.30 | 28.32 | 145.99 |
| NaOH | 0.00 | 0.00 | 0.00 |
| Xylan | 79.87 | 59.88 | 19.99 |
| Xylose | 444.92 | 382.63 | 62.29 |

The pre-hydrolysis process converts hemicellulose to monosaccharides by hydrolysis reactions. The majority of xylan portion is converted to xylose –the xylan content (substrate) decreased whereas the xylose content (product) increased. A small portion of cellulose is also converted to glucose -the cellulose and glucose content are in the same way as xylan and xylose, respectively. Both xylose and glucose are dissolved in the liquid phase. Unfortunately, xylose and glucose oligomers -incomplete hydrolyzed parts- appear. In addition, degradation products of pentose sugar (primarily furfural) are also formed. After the flash, water is removed 81.59%. In the separation section, the major significant component that appeared in the liquid (L-FTX) is xylose. On the other hand, the major component that appears in solid (S-FTX) is cellulose.

- Neutralization

Process flow diagram

After separation step, the liquid residue (L-FTX) from centrifuge (F2-XYL) was neutralized by $\text{Ca}(\text{OH})_2$ (LIME) in an isothermal reactor (NEU) at 50 °C and 1 atm to remove H_2SO_4 . Neutralized product (PD-NEU) was then flowed to a hydro cyclone -95% solid recovery- for separating solids -mainly gypsum- (PDG-HC) from liquids -mainly xylose- (XYL).

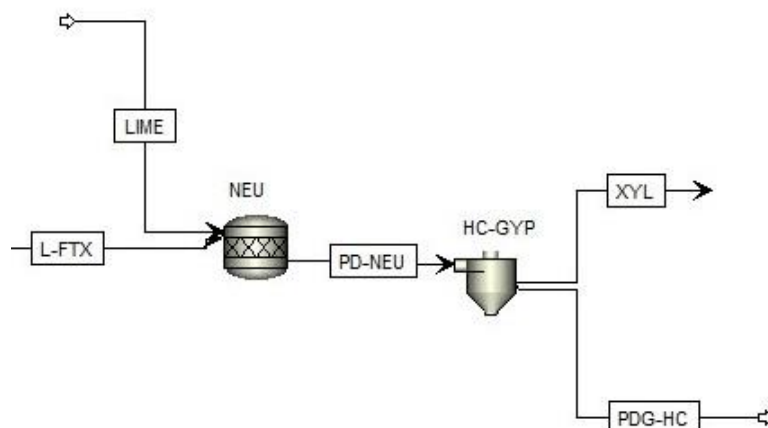


Figure 16. Process flow diagram of Neutralization

Process results

Table 16. Results of Neutralization

| Stream Name | LIME | PD-NEU | XYL | PDG-HC |
|--------------------------------|-------|----------|----------|--------|
| From | - | NEU | HC-GYP | HC-GYP |
| To | NEU | HC-GYP | HF2 | - |
| T (°C) | 25 | 50 | 50 | 50 |
| P (atm) | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 32.93 | 1,191.66 | 1,039.28 | 152.38 |
| Component | | | | |
| Ash | 0.00 | 22.83 | 1.14 | 21.69 |
| Xylose oli. | 0.00 | 10.63 | 10.42 | 0.21 |
| Glucose oli. | 0.00 | 9.00 | 8.82 | 0.18 |
| Ca(OH) ₂ | 32.93 | 0.00 | 0.00 | 0.00 |
| Cellulose | 0.00 | 122.46 | 91.35 | 31.12 |
| Enzyme | 0.00 | 0.00 | 0.00 | 0.00 |
| Furfural | 0.00 | 1.46 | 1.43 | 0.03 |
| Glucose | 0.00 | 45.02 | 44.12 | 0.90 |
| Gypsum | 0.00 | 76.51 | 3.83 | 72.69 |
| H ₂ O | 0.00 | 432.92 | 424.26 | 8.66 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 | 0.00 |
| HMF | 0.00 | 0.00 | 0.00 | 0.00 |
| LIGNIN | 0.00 | 28.32 | 20.77 | 7.55 |
| NaOH | 0.00 | 0.00 | 0.00 | 0.00 |
| Xylan | 0.00 | 59.88 | 58.17 | 1.70 |
| Xylose | 0.00 | 382.63 | 374.98 | 7.65 |

In the neutralization, H_2SO_4 in L-FTX reacts with $\text{Ca}(\text{OH})_2$ in LIME to form gypsum -solid phase- as appearing in PD-NEU. HC-GYP separates solids (PDG-HC) -containing gypsum- from liquids (XYL) –containing desired products.

- xylose purification

Process flow diagram

In order to make the xylose product purer, flash is required. Neutralized liquid was flashed at 1 atm and 110 °C – the maximum temperature for water removal without sugar decomposition.

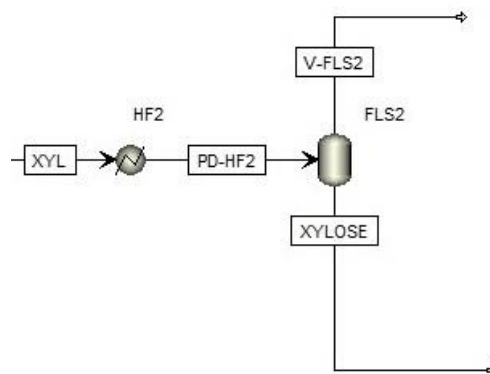


Figure 17. Process flow diagram of xylose purification

Process results

Table 17. Results of xylose Purification

| Stream Name | PD-HF2 | V-FLS2 | XYLOSE |
|--------------------------|----------|--------|--------|
| From | HF2 | FLS2 | FLS2 |
| To | FLS2 | - | |
| T (°C) | 110 | 109 | 109 |
| P (atm) | 1 | 1 | 1 |
| Flow (kg/hr) | 1,039.28 | 292.99 | 746.30 |
| Component | | | |
| Ash | 1.14 | 0.00 | 1.14 |
| Xylose oli. | 10.42 | 0.00 | 10.42 |
| Glucose oli. | 8.82 | 0.00 | 8.82 |
| $\text{Ca}(\text{OH})_2$ | 0.00 | 0.00 | 0.00 |
| Cellulose | 91.35 | 0.00 | 91.35 |
| Enzyme | 0.00 | 0.00 | 0.00 |
| Furfural | 1.43 | 0.89 | 0.54 |
| Glucose | 44.12 | 0.00 | 44.12 |
| Gypsum | 3.83 | 0.00 | 3.83 |

| Stream Name | PD-HF2 | V-FLS2 | XYLOSE |
|--------------------------------|--------|--------|--------|
| H ₂ O | 424.26 | 292.10 | 132.16 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 |
| HMF | 0.00 | 0.00 | 0.00 |
| LIGNIN | 20.77 | 0.00 | 20.77 |
| NaOH | 0.00 | 0.00 | 0.00 |
| Xylan | 58.17 | 0.00 | 58.17 |
| Xylose | 374.98 | 0.00 | 374.98 |

After the flash, water is removed 68.85%. The final product of xylose reaches 50.25 % with a flow rate of 746.30 kg/hr.

- Hydrolysis

Process flow diagram

The solid residue (S-FTX) from the centrifuge (FT-XYL) was then adjusted from 65 °C to 50 °C. Cellulase (ENZ) and water (HL-WATER) were prepared for hydrolysis conditions and then fed to the reactor. The hydrolysis reactor (HYDLYZ) operates at 50 °C and 1 atm. After that, a filter -95% solid recovery- was required to separate solids - non-hydrolyzed residue- (SOL-F3) from liquids -mainly glucose- (GLUCOSE).

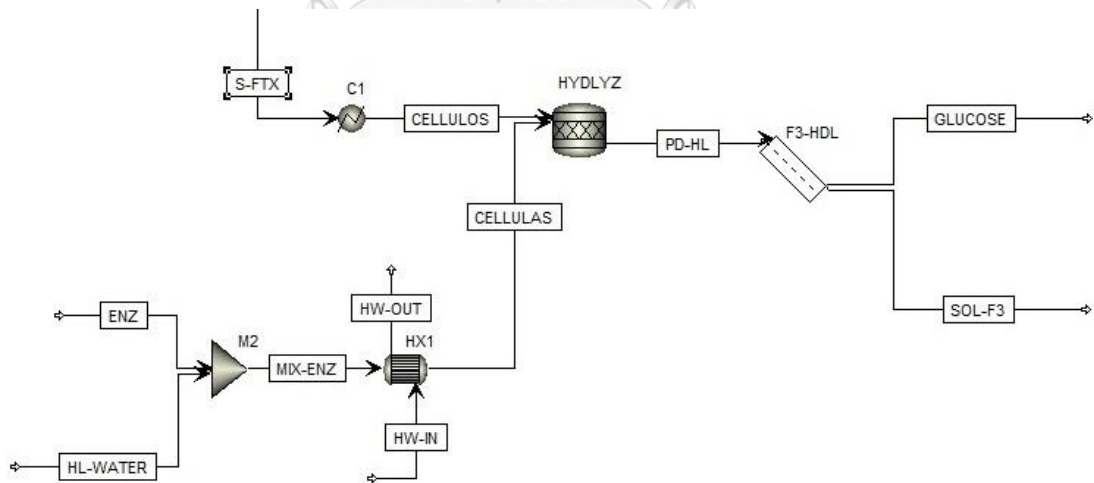


Figure 18. Process flow diagram of hydrolysis

Process results

Table 18. Results of enzyme preparation

| Stream Name | ENZ | HL-WATER | MIX-ENZ | CELLULAS |
|--------------------------------|------|----------|---------|----------|
| From | - | - | M2 | HX1 |
| To | M2 | M2 | HX1 | HYDLYZ |
| T (°C) | 25 | 25 | 25 | 50 |
| P (atm) | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 0.07 | 66.66 | 66.72 | 66.72 |
| Component | | | | |
| Ash | 0.00 | 0.00 | 0.00 | 0.00 |
| Xylose oli. | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose oli. | 0.00 | 0.00 | 0.00 | 0.00 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 | 0.00 |
| Cellulose | 0.00 | 0.00 | 0.00 | 0.00 |
| Enzyme | 0.07 | 0.00 | 0.07 | 0.07 |
| Furfural | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose | 0.00 | 0.00 | 0.00 | 0.00 |
| Gypsum | 0.00 | 0.00 | 0.00 | 0.00 |
| H ₂ O | 0.00 | 66.66 | 66.66 | 66.66 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 | 0.00 |
| HMF | 0.00 | 0.00 | 0.00 | 0.00 |
| LIGNIN | 0.00 | 0.00 | 0.00 | 0.00 |
| NaOH | 0.00 | 0.00 | 0.00 | 0.00 |
| Xylan | 0.00 | 0.00 | 0.00 | 0.00 |
| Xylose | 0.00 | 0.00 | 0.00 | 0.00 |

Cellulase is used as an enzyme catalyst for hydrolysis reactions. Cellulase is prepared prior to obtaining an operating condition before being added to the hydrolysis reactor.

Table 19. Results of hydrolysis

| Stream Name | CELLULOS | PD-HL | GLUCOSE | SOL-F3 |
|--------------|----------|----------|---------|--------|
| From | C1 | HYDLYZ | F3-HDL | F3-HDL |
| To | HYDLYZ | F3-HDL | - | - |
| T (°C) | 50 | 50 | 50 | 50 |
| P (atm) | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 1,350.95 | 1,417.67 | 735.63 | 682.04 |
| Component | | | | |
| Ash | 433.74 | 433.74 | 21.69 | 412.05 |
| Xylose oli. | 1.73 | 1.73 | 1.47 | 0.26 |

| Stream Name | CELLULOS | PD-HL | GLUCOSE | SOL-F3 |
|--------------------------------|----------|--------|---------|--------|
| Glucose oli. | 1.47 | 1.47 | 1.25 | 0.22 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 | 0.00 |
| Cellulose | 600.61 | 14.92 | 12.68 | 2.24 |
| Enzyme | 0.00 | 0.07 | 0.00 | 0.06 |
| Furfural | 0.24 | 0.24 | 0.20 | 0.04 |
| Glucose | 7.33 | 658.09 | 559.38 | 98.71 |
| Gypsum | 0.00 | 0.00 | 0.00 | 0.00 |
| H ₂ O | 70.48 | 72.06 | 61.25 | 10.81 |
| H ₂ SO ₄ | 7.10 | 7.10 | 6.03 | 1.06 |
| HMF | 0.00 | 0.00 | 0.00 | 0.00 |
| LIGNIN | 145.99 | 145.99 | 10.01 | 135.98 |
| NaOH | 0.00 | 0.00 | 0.00 | 0.00 |
| Xylan | 19.99 | 19.99 | 8.73 | 11.26 |
| Xylose | 62.29 | 62.29 | 52.95 | 9.34 |

The hydrolysis process converts cellulose into glucose by hydrolysis reactions. The ratio of cellulose: water in reactions is 1:1 mol and glucose is also formed at 1 mol. Glucose appeared as a main component in PD-HL- and other sugars dissolved in the liquid phase whereas ash and Lignin –second and third component in PD-HL- are still solid. Slurry (PD-HL) flows to the filter (F3-HDL) for separating liquids (GLUCOSE) from solids (SOL-F3). The final product of glucose reaches 76.04% with a flow rate of 735.63 kg/hr.

4.1.2 Economics

The expense, income, and economic parameters related to the plant investment of an alkaline pretreatment case under a project lifetime of 10 years and a payout period of 5 years are shown in the table below.

Table 20. Cost summary for alkaline pretreatment case

| Parameters | Cost |
|-----------------------------------|------------|
| Total Project Capital Cost (USD) | 14,147,556 |
| Total Operating Cost (USD/Yr) | 5,173,134 |
| Total Raw Materials Cost (USD/Yr) | 1,766,264 |
| Total Utilities Cost (USD/Yr) | 937,175 |
| Total Product Sales (USD/Yr) | 12,554,854 |
| Direct cost (USD) | 4,350,800 |
| Equipment cost (USD) | 2,249,300 |

Table 21. Value of economics parameters for alkaline pretreatment case

| Parameters | Value |
|---------------------|--------------|
| PI | 1.26 |
| IRR | 39.45 |
| NPV (USD) | 11,546,822 |
| Sugar cost (USD/kg) | Xylose 1.75 |
| | Glucose 0.36 |

Based on the process's expenses and income, the costs of xylose and glucose were calculated to be 1.75 and 0.36 USD/kg, respectively (pay out period of 5 years are assumed). This capital cost results in PI and IRR calculations of 1.26 and 39.45, respectively, indicating that the project should be invested. In terms of NPV of 11,546,822 USD, the process is profitable. Further, the costs of sugar available in the market are about 2.85 and 0.59 USD/kg for Xylose and Glucose [26] which are comparable to the costs determined in this work

4.2 Acid pretreatment case

4.2.1 Simulation

- Acid pretreatment

Process flow diagram

OPEFB (LIGNO-I) and water (PT-WATER) with the same ratio and flow rate as in the alkaline pretreatment case were used. Then, mixtures (LIGNO-O) were fed to a pretreatment reactor (APRET) and performed at a concentration of 1.1%(v/v) of sodium hydroxide, 120 °C and 1 atm.

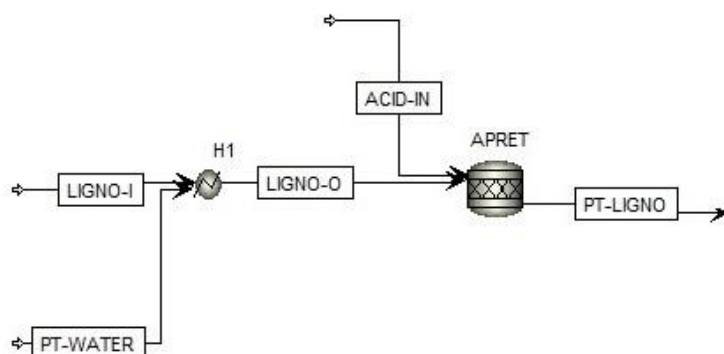


Figure 19. Process flow diagram of acid pretreatment

Process results

Table 22. Results of acid pretreatment

| Stream Name | LIGNO-I | PT-WATER | LIGNO-O | ACID-IN | PT-LIGNO |
|--------------------------------|----------|-----------|-----------|---------|-----------|
| From | - | - | H1 | - | APRET |
| To | H1 | H1 | APRET | APRET | NEU |
| T (°C) | 25 | 25 | 120 | 120 | 120 |
| P (atm) | 1 | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 3,000.00 | 36,000.00 | 39,000.00 | 61.06 | 39,061.06 |
| Component | | | | | |
| Ash | 480.60 | 0.00 | 480.60 | 0.00 | 480.60 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cellulose | 1,142.70 | 0.00 | 1,142.70 | 0.00 | 1,142.70 |
| Furfural | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Gypsum | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| H ₂ O | 0.00 | 36,000.00 | 36,000.00 | 0.23 | 36,000.23 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 | 60.83 | 60.83 |
| HMF | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| LIGNIN | 478.80 | 0.00 | 478.80 | 0.00 | 478.80 |
| Xylan | 897.90 | 0.00 | 897.90 | 0.00 | 897.90 |
| Xylose | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

For acid pretreatment, the lignin is removed as well, but appears in a different phase with alkaline pretreatment. Lignin and cellulose are in a solid phase, whereas hemicellulose is in a liquid phase. At this stage, the two phases are still mixed.

- Feed preparation

Process flow diagram

The pretreated OPEFB (PT-LIGNO) was neutralized by Ca(OH)₂ (LIME) at 50 °C and 1 atm to removed acid pretreatment chemicals. Next, flash (FLS0) was used to remove the water so that it didn't load in the separation process. After that, the desirable liquid phase (LIQ-F1) was recovered by centrifuge - 95% solid recovery and 20% moisture. Then, sulfuric acid (PH-ACID) was fed to a concentration of 0.1%(w/w) and heated to a pre-hydrolysis condition.

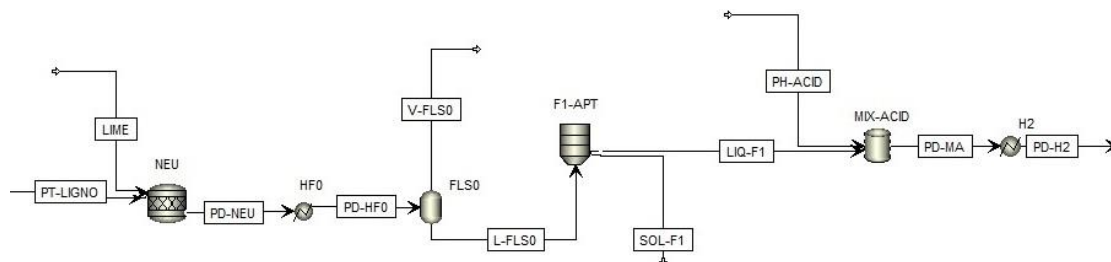


Figure 20. Process flow diagram of feed preparation

Process results

Table 23. Results of feed preparation (1)

| Stream Name | LIME | PD-NEU | PD-HF0 | V-FLS0 | L-FLS0 |
|--------------------------------|-------|-----------|-----------|-----------|-----------|
| From | - | NEU | HF0 | FLS0 | FLS0 |
| To | NEU | HF0 | FLS0 | - | F1-APT |
| T (°C) | 50 | 50 | 100 | 100 | 100 |
| P (atm) | 1 | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 46.89 | 39,107.95 | 39,107.95 | 28,800.18 | 10,307.77 |
| Component | | | | | |
| Ash | 0.00 | 480.60 | 480.60 | 0.00 | 480.60 |
| Ca(OH) ₂ | 46.89 | 0.93 | 0.93 | 0.00 | 0.93 |
| Cellulose | 0.00 | 1,142.70 | 1,142.70 | 0.00 | 1,142.70 |
| Furfural | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Gypsum | 0.00 | 106.79 | 106.79 | 0.00 | 106.79 |
| H ₂ O | 0.00 | 36,000.23 | 36,000.23 | 28,800.18 | 7,200.05 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| HMF | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| LIGNIN | 0.00 | 478.80 | 478.80 | 0.00 | 478.80 |
| Xylan | 0.00 | 897.90 | 897.90 | 0.00 | 897.90 |
| Xylose | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

Table 24. Results of feed preparation (2)

| Stream Name | LIQ-F1 | SOL-F1 | PH-ACID | PD-MA | PD-H2 |
|--------------|----------|----------|----------|----------|----------|
| From | F1-APT | F1-APT | - | MIX-ACID | H2 |
| To | MIX-ACID | | MIX-ACID | H2 | HDL |
| T (oC) | 100 | 100 | 25 | 108 | 140 |
| P (atm) | 1 | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 8,144.28 | 2,163.49 | 109.62 | 8,253.90 | 8,253.90 |
| Component | | | | | |
| Ash | 24.03 | 456.57 | 0.00 | 24.03 | 24.03 |

| Stream Name | LIQ-F1 | SOL-F1 | PH-ACID | PD-MA | PD-H2 |
|--------------------------------|----------|--------|---------|----------|----------|
| Ca(OH) ₂ | 0.00 | 0.93 | 0.00 | 0.00 | 0.00 |
| Cellulose | 193.67 | 949.03 | 0.00 | 193.67 | 193.67 |
| Furfural | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Gypsum | 5.34 | 101.45 | 0.00 | 5.34 | 5.34 |
| H ₂ O | 7,048.05 | 152.00 | 2.19 | 7,050.24 | 7,050.24 |
| H ₂ SO ₄ | 0.00 | 0.00 | 107.43 | 107.43 | 107.43 |
| HMF | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| LIGNIN | 23.94 | 454.86 | 0.00 | 23.94 | 23.94 |
| Xylan | 849.25 | 48.65 | 0.00 | 849.25 | 849.25 |
| Xylose | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

As a result, hemicellulose is the major component that can be converted to monomeric sugar. PT-LIGNO should first remove H₂SO₄ -which is also liquid. Ca(OH)₂ (LIME) is required to react with H₂SO₄ in PT-LIGNO to form gypsum, -which is solid. Flash (FLS0) removes 80.00% of water from PT-LIGNO. Next, F1-APT is required to separate LIQ-F1 -mainly water and hemicellulose- from SOL-F1. The desired liquid phase (LIQ-F1) is then mixed with H₂SO₄ for hydrolysis (PH-ACID), and the temperature is raised to 140 °C.

- Acid hydrolysis

Process flow diagram

The prepared feed (PD-H2) was hydrolyzed in an isothermal reactor (HDL) at 140 °C and 1 atm. The product from hydrolysis (PD-HDL) was cooled and flashed (FLS1) at 102 °C.

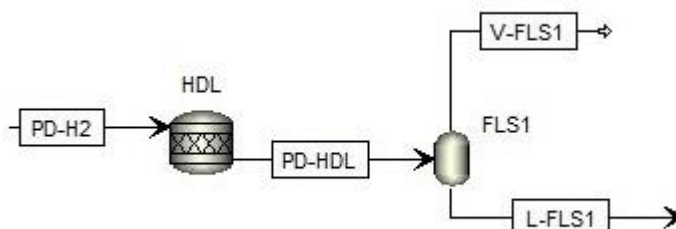


Figure 21 Process flow diagram of acid hydrolysis

Process results

Table 25. Results of acid hydrolysis

| Stream Name | PD-HDL | V-FLS1 | L-FLS1 |
|--------------------------------|----------|----------|----------|
| From | HDL | FLS1 | FLS1 |
| To | FLS1 | - | NEU2 |
| T (°C) | 140 | 102 | 102 |
| P (atm) | 1 | 1 | 1 |
| Flow (kg/hr) | 8,253.90 | 5,714.58 | 2,539.32 |
| Component | | | |
| Ash | 24.03 | 0.00 | 24.03 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 |
| Cellulose | 174.74 | 0.00 | 174.74 |
| Furfural | 48.66 | 45.02 | 3.64 |
| Glucose | 20.70 | 0.00 | 20.70 |
| Gypsum | 5.34 | 0.00 | 5.34 |
| H ₂ O | 6,981.71 | 5,669.50 | 1,312.20 |
| H ₂ SO ₄ | 107.43 | 0.05 | 107.38 |
| HMF | 0.23 | 0.00 | 0.23 |
| LIGNIN | 23.94 | 0.00 | 23.94 |
| Xylan | 160.63 | 0.00 | 160.63 |
| Xylose | 706.48 | 0.00 | 706.48 |

The hydrolysis process converts hemicellulose to xylose by hydrolysis reactions. Most of the xylan portion is converted to xylose. Xylose is soluble in a liquid phase. Due to the small amount of cellulose, it is neglected. In addition, degradation products (furfural and HMF) are also formed. After the flash, water is removed 81.21%.

- Neutralization and purification

Process flow diagram

The liquid residue (L-FLS1) from flash (FLS1) was neutralized again by Ca(OH)₂ (LIME2) in isothermal reactor (NEU2) at 50 °C and 1 atm to remove H₂SO₄ from hydrolysis. Neutralized product (PD-NEU2) was then separate by hydro cyclone -95% solid recovery- to remove solid -mainly gypsum- (GYPSUM) from liquid -mainly xylose- (SG). Flash (FLS2) was required to operate at 104 °C for increasing sugar concentration.

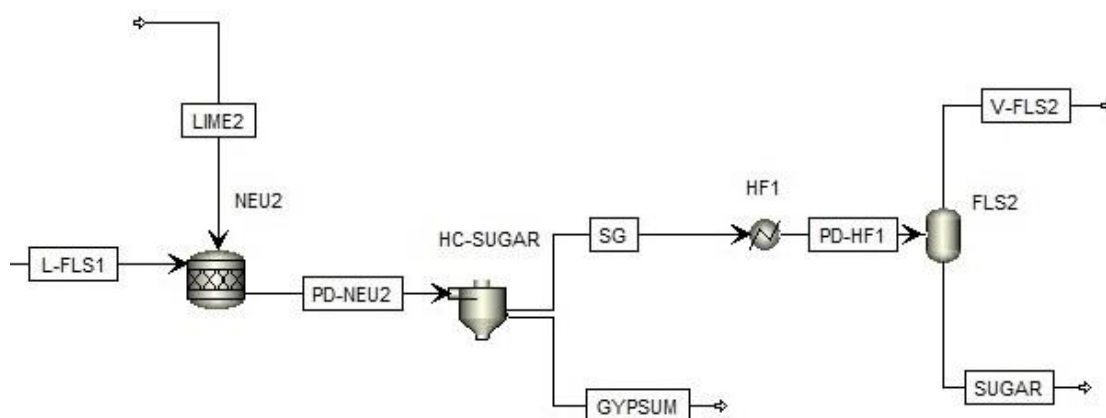


Figure 22. Process flow diagram of neutralization and purification

Process results

Table 26. Results of neutralization

| Stream Name | LIME2 | PD-NEU2 | SG | GYPSUM |
|--------------------------------|-------|----------|----------|----------|
| From | - | NEU2 | HC-SUGAR | HC-SUGAR |
| To | NEU2 | HC-SUGAR | HF1 | - |
| T (oC) | 50 | 50 | 50 | 50 |
| P (atm) | 1 | 1 | 1 | 1 |
| Flow (kg/hr) | 81.15 | 2,620.47 | 2,347.34 | 273.14 |
| Component | | | | |
| Ash | 0.00 | 24.03 | 1.20 | 22.83 |
| Ca(OH) ₂ | 81.15 | 0.04 | 0.00 | 0.03 |
| Cellulose | 0.00 | 174.74 | 133.49 | 41.25 |
| Furfural | 0.00 | 3.64 | 3.64 | 0.00 |
| Glucose | 0.00 | 20.70 | 20.70 | 0.00 |
| Gypsum | 0.00 | 193.84 | 9.69 | 184.15 |
| H ₂ O | 0.00 | 1,312.20 | 1,312.20 | 0.00 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 | 0.00 |
| HMF | 0.00 | 0.23 | 0.23 | 0.00 |
| LIGNIN | 0.00 | 23.94 | 1.20 | 22.74 |
| Xylan | 0.00 | 160.63 | 158.50 | 2.13 |
| Xylose | 0.00 | 706.48 | 706.48 | 0.00 |

In the neutralization, H₂SO₄ in L-FLS1 reacts with Ca(OH)₂ in LIME2 to form gypsum -solid phase- as appeared in PD-NEU2. HC-SUGAR is separated into solids (GYPSUM) from liquid (SG) – mainly containing xylose.

Table 27. Results of purification

| Stream Name | PD-HF1 | SUGAR | V-FLS2 |
|--------------------------------|----------|----------|--------|
| From | HF1 | FLS2 | FLS2 |
| To | FLS2 | - | - |
| T (oC) | 106 | 106 | 106 |
| P (atm) | 1 | 1 | 1 |
| Flow (kg/hr) | 2,347.34 | 1,403.88 | 943.45 |
| Component | | | |
| Ash | 1.20 | 1.20 | 0.00 |
| Ca(OH) ₂ | 0.00 | 0.00 | 0.00 |
| Cellulose | 133.49 | 133.49 | 0.00 |
| Furfural | 3.64 | 0.91 | 2.74 |
| Glucose | 20.70 | 20.70 | 0.00 |
| Gypsum | 9.69 | 9.69 | 0.00 |
| H ₂ O | 1,312.20 | 371.49 | 940.72 |
| H ₂ SO ₄ | 0.00 | 0.00 | 0.00 |
| HMF | 0.23 | 0.23 | 0.00 |
| LIGNIN | 1.20 | 1.20 | 0.00 |
| Xylan | 158.50 | 158.50 | 0.00 |
| Xylose | 706.48 | 706.48 | 0.00 |

After the flash, water is removed 71.69%. Xylose -which is the desired product- reaches 50.32% and its flow rate is 1403.88 kg/hr.

4.2.2 Economics

The expense, income, and economic parameters associated to the plant investment of an acid pretreatment case under a project lifetime of 10 years and a payout period of 5 years are shown in the table below.

Table 28. Cost summary for acid pretreatment case

| Parameters | Cost |
|-----------------------------------|------------|
| Total Project Capital Cost (USD) | 9,872,241 |
| Total Operating Cost (USD/Yr) | 6,123,895 |
| Total Raw Materials Cost (USD/Yr) | 2,378,400 |
| Total Utilities Cost (USD/Yr) | 1,547,584 |
| Total Product Sales (USD/Yr) | 11,463,792 |
| Direct cost (USD) | 2,924,700 |
| Equipment cost (USD) | 1,154,400 |

Table 29. Value of economics parameters for acid pretreatment case

| Parameters | Value |
|---------------------|-----------|
| PI | 1.21 |
| IRR | 39.49 |
| NPV (USD) | 8,638,133 |
| Sugar cost (USD/kg) | 0.46 |

From the expenses and income of the process, the cost of xylose is estimated to be 0.46 USD/kg. This cost of xylose results in PI and IRR values equal to 1.21 and 39.49, respectively, indicating that the project deserves investment and is profitable with the NPV of 8,638,133 USD.

4.3 Comparison the process using alkaline and acid pretreatment

The main highlight of an alkaline pretreatment case is that two types of sugar, xylose and glucose, are produced separately. The flow rate of two sugars are approximately the same (fig.23). When considering the concentration, the concentration of glucose is slightly higher (fig.24). In contrast, acid pretreatment yields only one product, xylose, at a concentration comparable to that of alkaline pretreatment (fig.24). However, it has the advantage of having nearly twice the volume of the alkaline pretreatment (fig.23).

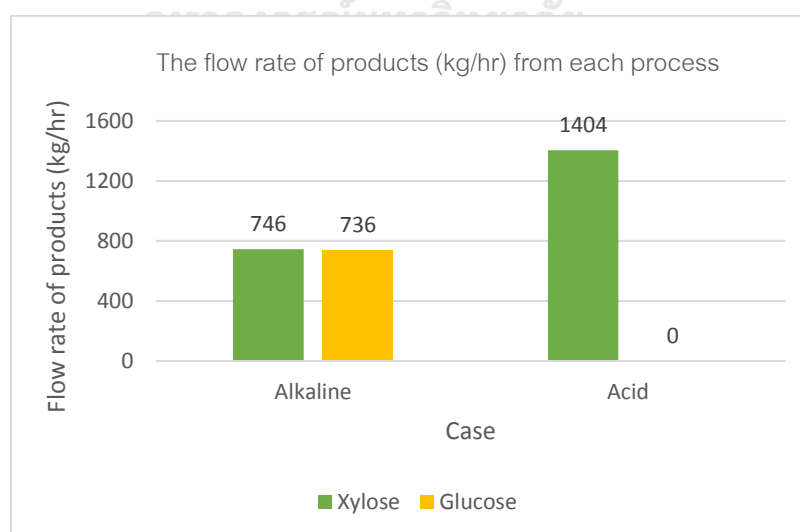


Figure 23. The flow rate of products of alkaline and acid pretreatment case

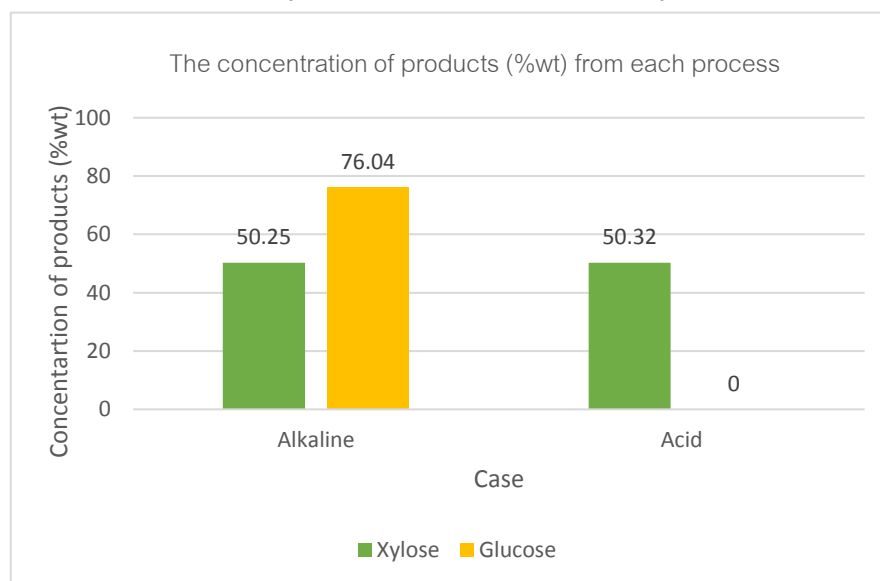


Figure 24. The concentration of products from alkaline and acid pretreatment case

Economics analysis part, Alkaline pretreatment two sugars are produced, making the process even more complicated. The process requires a lot of equipment for 2-stage hydrolysis, obtaining xylose in the first stage and glucose in the second stage. Besides that, numerous separation units are also necessary because the liquid phase product has to be separated from the desired materials, hemicellulose and cellulose, or impurities in the solid phase, primarily separating xylose from cellulose. For these reasons, the cost of equipment and investment cost are higher (fig.25), which is considered to be a weak point of the process. However, since both glucose and xylose can be sold due to the two-step sugar production process, the PI and NPV of the alkaline pretreatment case is higher (fig.26, fig.27). The IRR are not significant different (fig.28).

In contrast, acid pretreatment results in a single desired material. Moreover, it's in the liquid phase. So, hydrolysis is only one stage. Furthermore, it requires less equipment. Although the number of neutralizations and subsequent separations is greater, the low quantity of the substance makes the equipment small and less expensive. As a result of this factor, the cost of equipment and investment cost are low

(Fig.25), which is an advantage of the process. The IRR is similar to alkaline pretreatment case (fig.28). Unfortunately, it has a lower PI and NPV (fig.26, fig.27). The project's revenue only depends on xylose, which is; therefore, a limitation of the process.

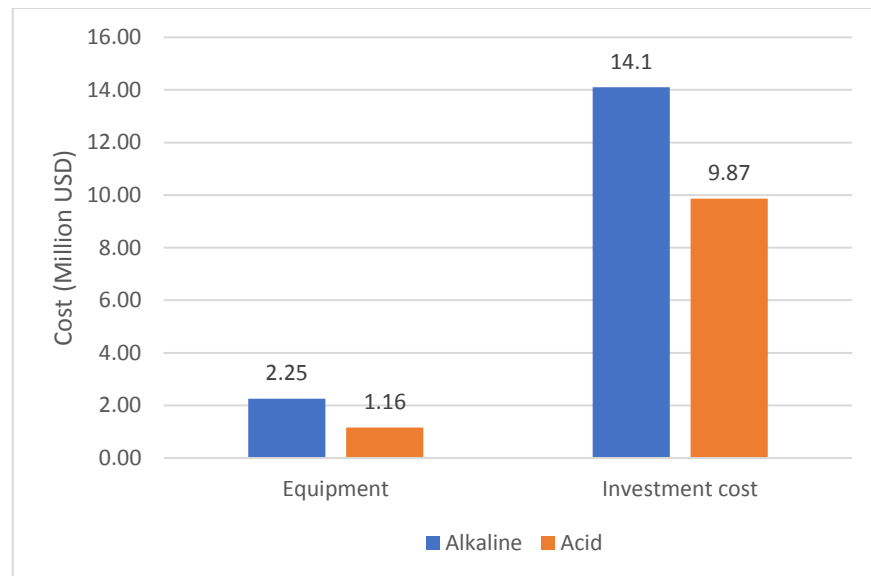


Figure 25. The equipment and investment cost of alkaline and acid pretreatment case

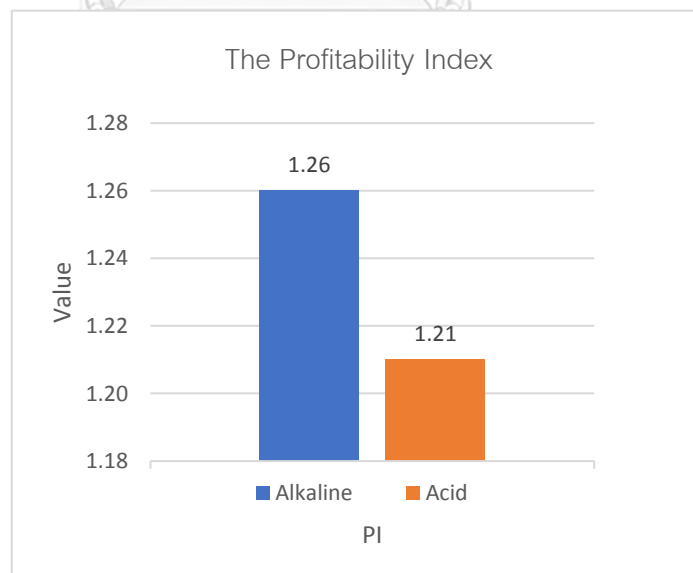


Figure 26. The profitability index of alkaline and acid pretreatment case

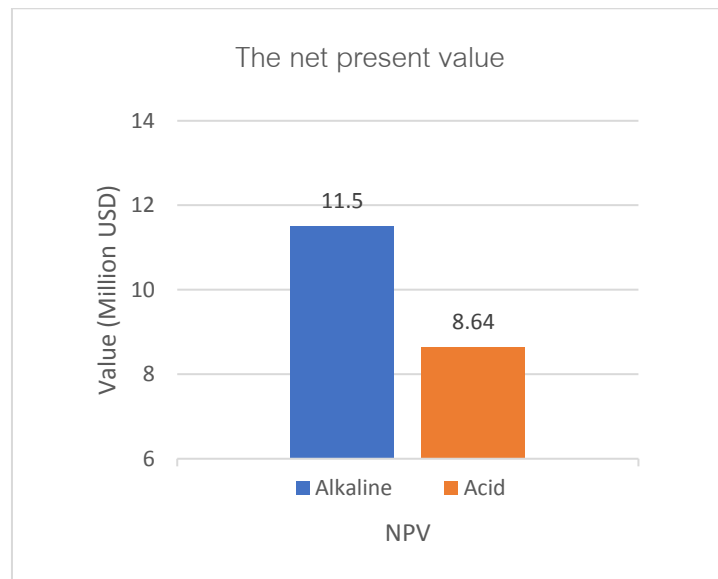


Figure 27. The net present value of alkaline and acid pretreatment case

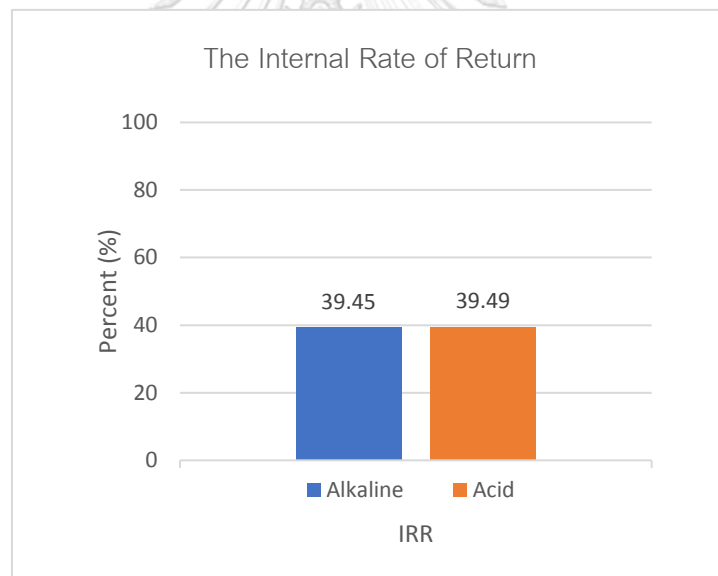


Figure 28. The internal rate of return of alkaline and acid pretreatment case

Chapter 5

Conclusion

5.1 Effect of different pretreatment chemicals

A comparison of the effects of different pretreatment chemicals revealed that both pretreatment chemicals can alter the structure of lignocellulose. However, the pretreated materials are in a different state. In the case of alkaline pretreatment, alkaline is capable of separating both hemicellulose and cellulose (both xylose and glucose are eventually obtained), which are still in the solid phase whereas lignin, an undesirable component dissolves into the liquid phase. Therefore, the phase that needs to be processed further is the solid phase. In the case of acid pretreatment, acid can degrade lignocellulose structures, releasing only hemicellulose (only xylose is eventually obtained). In the liquid phase, the pretreated hemicellulose dissolves whereas lignin and cellulose are in the solid phase. This acid pretreatment results in the loss of cellulose, a valuable component.

5.2 Subsequent processes after pretreatment

Because the desired products in both cases are in different phases. As a result, the subsequent processes are different as well.

In the alkaline pretreatment, the pretreated feed contains both hemicellulose and cellulose that can be utilized. Therefore, the process is designed to enable the cost-effective use of these two substances. The designed process uses hydrolysis reactions to convert hemicellulose and cellulose into xylose and glucose, respectively. However, there are different stages so that the two types of sugar can be easily separated from each other. After the pretreatment, acid hydrolysis is primarily used to digest hemicellulose into xylose, which is dissolved in liquid and then separated first. Followed by enzymatic hydrolysis, cellulase was used to convert the solid cellulose into glucose which was dissolved in the liquid phase. Finally, the product from the alkaline pretreatment case yields both xylose, which is 50.25%, and liquid glucose, which is 76.04%. Moreover, they are produced separately.

In the acid pretreatment case, the feed for hydrolysis contains mainly hemicellulose and a small portion of cellulose. The cellulose attached to lignin is ignored because it is difficult to extract and lower cost of product. Thus, acid hydrolysis was chosen to convert hemicellulose to xylose, which is a higher value product. So, the only one product from this case is xylose at concentration of 50.32% wt.

5.3 Economics analysis

According to the economics analysis for both projects, the process design through the acid pretreatment has a low investment cost, which is 9,872,241 USD, due to the low complexity of the process. As a result, the capital cost of sugar, which is 0.46 USD/kg, is low. While the alkaline pretreatment case is more complicated. As a result, the investment cost, which is 14,147,556 USD, is high, and the capital cost of xylose and glucose, which are 1.75 and 0.36 USD/kg, respectively, are also high. However, this process does not rely solely on xylose, allowing for greater flexibility and adaptability during periods of xylose price fluctuation. Further, in terms of NPV, the process with alkaline pretreatment yields higher NPV than the process with the acid pretreatment (11,546,822 USD VS 8,638,133 USD). Again, this reflects from being able to sell both xylose and glucose via the alkaline pretreatment process.

5.4 Recommendation

5.4.1 Alkaline pretreatment case

- This process is suitable for investments with high capital and high profit margins
- There are two types of products that can accommodate the risk of xylose price fluctuations.
- The produced sugars are suitable as a starting material for the production of other valuable chemicals because these processes do not require high purity of sugar.
- The sugar concentration can be increased with a more efficient separation process.

5.4.2 Acid pretreatment case

- This process is suitable for investments with low capital and required only xylose products.
- The produced xylose is proper as a starting material for the production of other valuable chemicals for the same reason as the alkaline case.
- The process can be enriched by further development of cellulose process.



Appendix

1 U: 1 g cellulose was digested into 0.04 g glucose in 1 hr.

Basis: 100 g cellulose

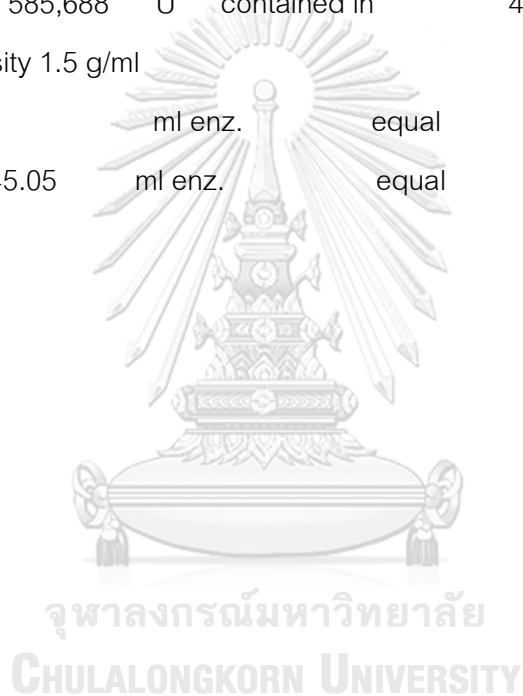
| | | | | |
|---------|-------------|----------|---------|---|
| 1 | g cellulose | required | 1 | U |
| 585,688 | g cellulose | required | 585,688 | U |

enzyme activity 13,000 U/ml

| | | | | |
|---------|---|--------------|-------|---------|
| 13,000 | U | contained in | 1 | ml enz. |
| 585,688 | U | contained in | 45.05 | ml enz. |

enzyme density 1.5 g/ml

| | | | | |
|-------|---------|-------|-------|--------|
| 1 | ml enz. | equal | 1.5 | g enz. |
| 45.05 | ml enz. | equal | 67.58 | g enz. |



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