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Process simulation of Kraft lignin oxidation for vanillin production

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ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ปีการศึกษา 2559 ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

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NAWAPORN KHWANJAISAKUN: Process simulation of Kraft lignin oxidation for vanillin production. ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: ASST. PROF. SUKSUN AMORNRAKSA, Ph.D., 135 pp.

Kraft lignin waste generated from Kraft pulping process can be potentially converted to a high value product such as vanillin. This work focused on feasibility study of vanillin production from Kraft lignin by oxidation reaction. A reaction model of Kraft lignin oxidation used in this work was selected from literature. The model was simulated by using MATLAB® software and many operating parameters such as feed concentration of Kraft lignin, reaction temperature, and oxygen partial pressure were optimized to obtain the highest yield of vanillin product. Then, three different separation methods i.e. vacuum distillation, solvent extraction, and solvent extraction followed by distillation were developed and compared in order to find the most suitable separation process for vanillin production. The simulation and comparison of different separation methods were done by using Aspen Plus® software. The result showed that the highest yield of vanillin at 9.25% could be obtained by using feed concentration of Kraft lignin at 30 grams/liter, temperature of 110 ^{o}C, and oxygen partial pressure of 5 bars. The solvent extraction followed by distillation was found to be the most suitable separation method as it required low energy consumption and offered the lowest production cost. The economic analysis showed that in the best case, payback period and IRR of the vanillin production from Kraft lignin are 6.14 years and 22.96%, respectively.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
Academic Year:	2016	Co-Advisor's Signature	....

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CHAPTER I

INTRODUCTION

1.1 General introduction

Kraft pulping process is a well-known process in chemical pulping production. It accounts more than 80% of global chemical pulp production capacity in 2015 [1]. The global chemical pulp production has been developed continually. Nowadays, the total global chemical pulp production capacity is approximately 115 million tonnes per year in 2015 and it is projected to increase to 122 million tonnes per year in 2019 [1]. That large amount of chemical pulping production generate approximately the same amount of black liquor.

Table 1-1 Black liquor composition [2]

Organic compound	% weight
Lignin	29-45
Hydroxy acids	25-35
Extractives	3-5
Formic acid	≈5
Acetic acid	≈3
Methanol	≈1

The composition of organic in black liquor is shown in Table 1-1. According to the table, the largest portion of black liquor is lignin. Lignin that is separated from black liquor from Kraft pulping process is called Kraft lignin. The Kraft lignin is a by-product from pulping process that has a potential to be utilized or converted into more valuable products. The utilization of Kraft lignin can be found in many pathways such as oxidation reaction to give vanillin and syringaldehyde, pyrolysis to give light oil, heavy oil, char and gas, and hydrogenolysis reaction to give phenol, guaiacol and others.

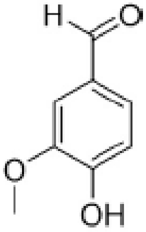


Figure 1-1 Vanillin structure [3]

Vanillin is a very interesting phenolic compound because it has a high market value and a large demand from food, perfumery and pharmaceutical industries. The current global demand for vanillin is estimated to be around 20,000 tons per year [4]. Vanillin is the phenolic compound that has structure as shown in Figure 1-1.

There are two types of vanillin in the market that are natural vanillin and synthetic vanillin. For natural vanillin, it is extracted from vanillin orchid pods that has quantity around 1% of total vanillin production [3]. For synthetic vanillin, there are main two pathways to produce it which are petroleum-based pathway and bio-based pathway. For the petroleum based pathway, raw material is guaiacol that has quantity around 85% of synthesis vanillin production [3]. For the bio-based pathway, vanillin is produced from lignin. The bio-based pathway is interesting. Today, maximum vanillin yield that can be obtained from lignin oxidation of nitrobenzene is around 13% w/w [5] and the maximum vanillin yield from batch oxidation of Kraft lignin with oxygen is around 10% w/w [6]. With plenty of potential lignin supply from the Kraft pulping process, it is very interesting and a good opportunity to study and find a method to produce vanillin from the Kraft lignin.

1.2 Research objectives

- To design and develop a simulation model for the vanillin production from Kraft lignin by direct oxidation method based on data from literatures.
- To find the optimal process conditions of Kraft lignin oxidation in batch reactor to produce maximum vanillin yield from the developed simulation model.

- To determine a suitable method for vanillin separation and study the economics of the developed processes by techno-economic analysis method.

1.3 Scopes of the research

- The mathematic model for Kraft lignin oxidation in batch reactor will be simulated by using MATLAB® program
- The operating process parameters to be optimized in this study are as follows.
    - Oxygen partial pressure
    - Initial concentration of feed lignin
    - Reaction temperature
- The design and simulation of the Kraft lignin oxidation production process will be conducted by using ASPEN Plus® program, based on the optimized process conditions obtained from the MATLAB® program.
- Finding the most suitable method to separate vanillin from products stream.
- The techno-economic analysis is used for economical consideration of all processes included production and separation process.

CHAPTER II

THEORY AND LITERATURE REVIEWS

This chapter explains in details of Kraft lignin, vanillin, Kraft lignin oxidation to obtain vanillin and other high value aromatic compound products.

2.1 Paper production process

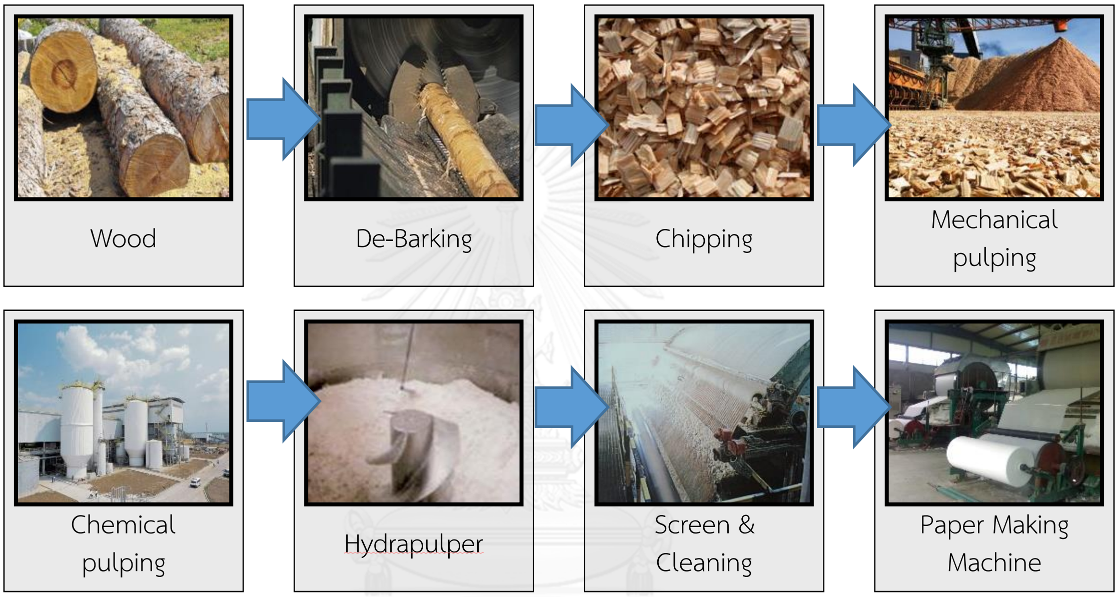


Figure 2-1 Paper production process

Nowadays, the paper production capacity is increasing every year. The process step is shown in Figure 2-1. The main raw material for paper production is wood. This process starts with preparation of raw material by removing bark and contaminates before sending wood to crush. After that, wood chip is sent to mechanical pulping process to separate fibres from wood chip by mechanical forces. Mechanical pulp gives paper that has opacity surface and yellowish/ grey tone color but the quality is still not good enough to make high quality paper. So, the mechanical pulp is fed to chemical pulping process to improve quality. Lignin in mechanical pulp is separated by cooking the mechanical pulp with chemicals solution. After that, chemical pulp is sent to screening and cleaning process to improve pulp quality and send to paper machine for making paper.

2.1.1 Chemical pulping process

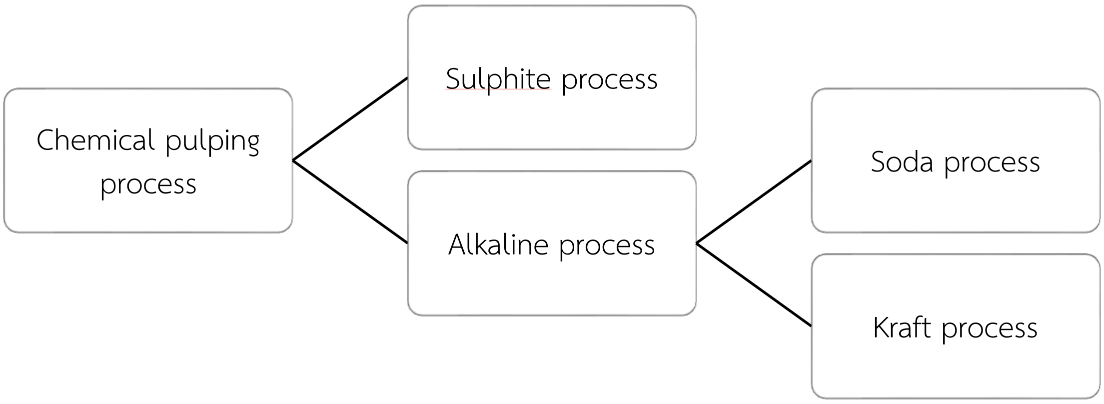


Figure 2-2 Paper production process [7]

From Figure 2-2, chemical pulping process can be separated into two main types. They are sulphite process and alkaline process. The sulphite process uses acid and bi-sulphite solution as cooking liquor for reacting with pulp from mechanical process in order to separate impurities in pulp. This process is always used to digest hard wood and some appropriate type of wood only. Pulp from this process has low strength property. The alkaline process consists two sub-group processes that are Soda process and Kraft process. The cooling liquor of Soda process is sodium hydroxide. This process is suitable for pulp that is used for making printing paper, letter paper and paper that want the softness. The Kraft process uses sodium hydroxide and sodium sulfide as the cooking liquor. This process gives stronger pulp compared to the Soda process. Nowadays, the Kraft pulping process accounts for more than 80% of total global chemical pulp production in 2015 [1].

2.1.2 Kraft pulping process

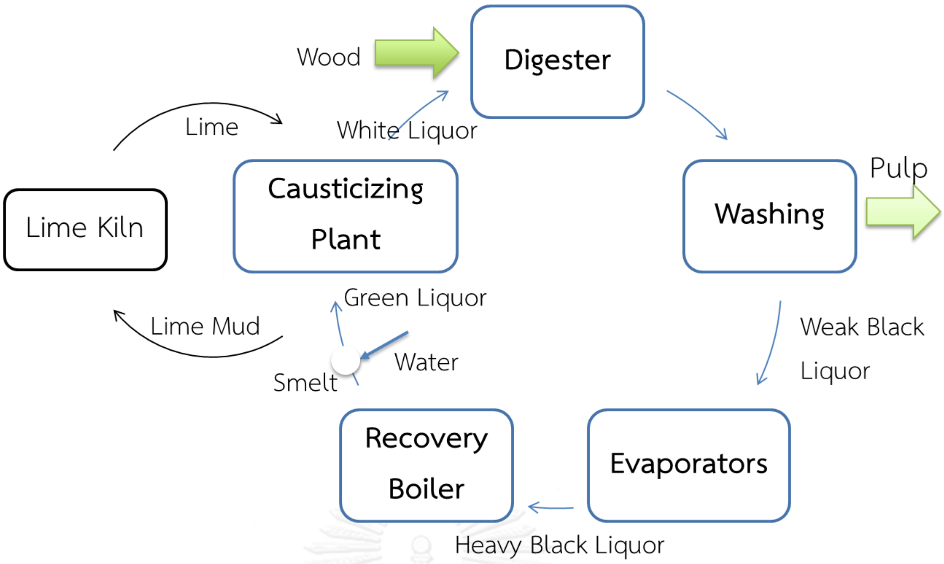


Figure 2-3 Kraft pulping process [2]

From Figure 2-3, Kraft pulping process starts with feeding wood chip from mechanical pulping process to a digester. Wood chip is digested by Sodium Hydroxide (NaOH) and Sodium Sulfide (Na_2S). The combination of both chemicals are called white liquor. The reaction is shown as below.

$$NaOH + Na_2S + \text{Wood chip} \rightarrow Na_2SO_4 + Na_2CO_3 + Pulp$$

From that reaction, the main compositions of pulp product from digester are cellulose and black liquor. The pulp product is then separated from the black liquor in the washing section. The black liquor containing lignin, acids, and some impurities as shown in Table 1-1 is sent to evaporators, to evaporate water and recover solvent for reuse again in digester. The output from the evaporators is known as heavy black liquor. However, it will have problem if we directly feed the heavy black liquor to a recovery boiler because the contained lignin and other solids will clog at the wall of recovery boiler, resulting in decreased efficiency of recovery boiler. So, lignin must be separated from the black liquor before feeding to recovery boiler. And the lignin that is separated here is called Kraft lignin.

2.2 Kraft lignin

Kraft lignin is the name of lignin that is produced from Kraft pulping process. Kraft pulping process produces large amount of black liquor. This liquor contains organic and inorganic part. The biggest amount in inorganic part is lignin that accounts for around 30% of total dry solid in black liquor.

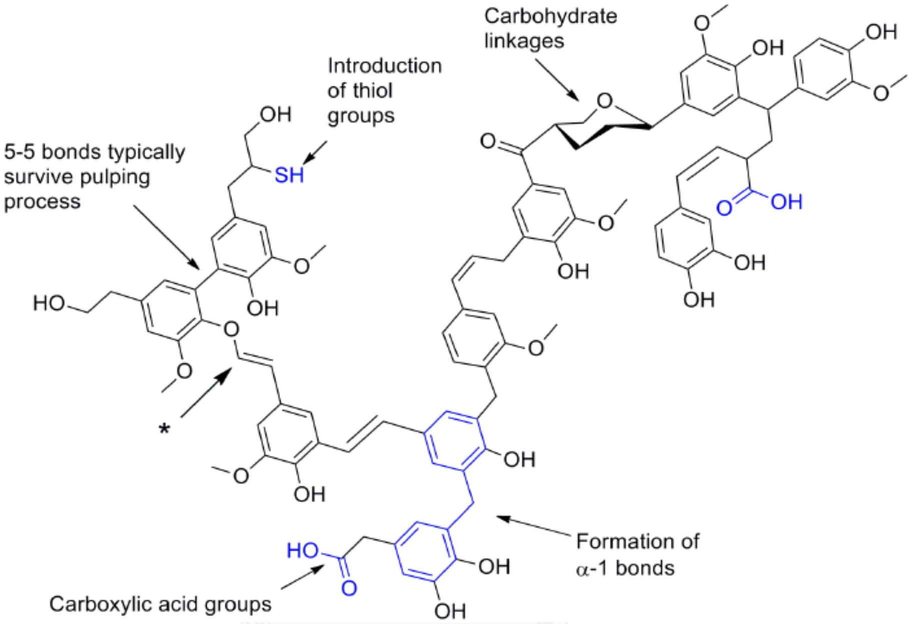


Figure 2-4 Model depicting structural features characteristic of Kraft pine lignin. [8]

The structure of Kraft lignin is shown in Figure 2-4. Kraft lignin is a network of aromatic structure.

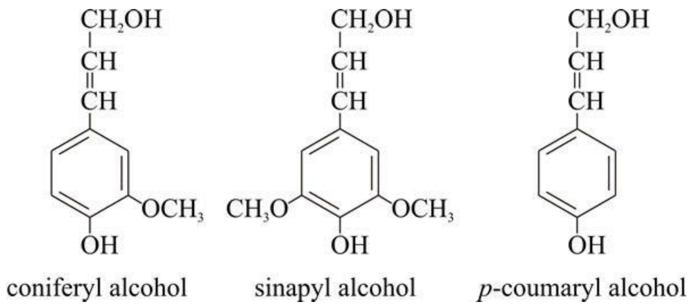


Figure 2-5 Main components of lignin

Normally, every type of lignin has the same thee main components. They are coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol are shown in Figure 2-5.

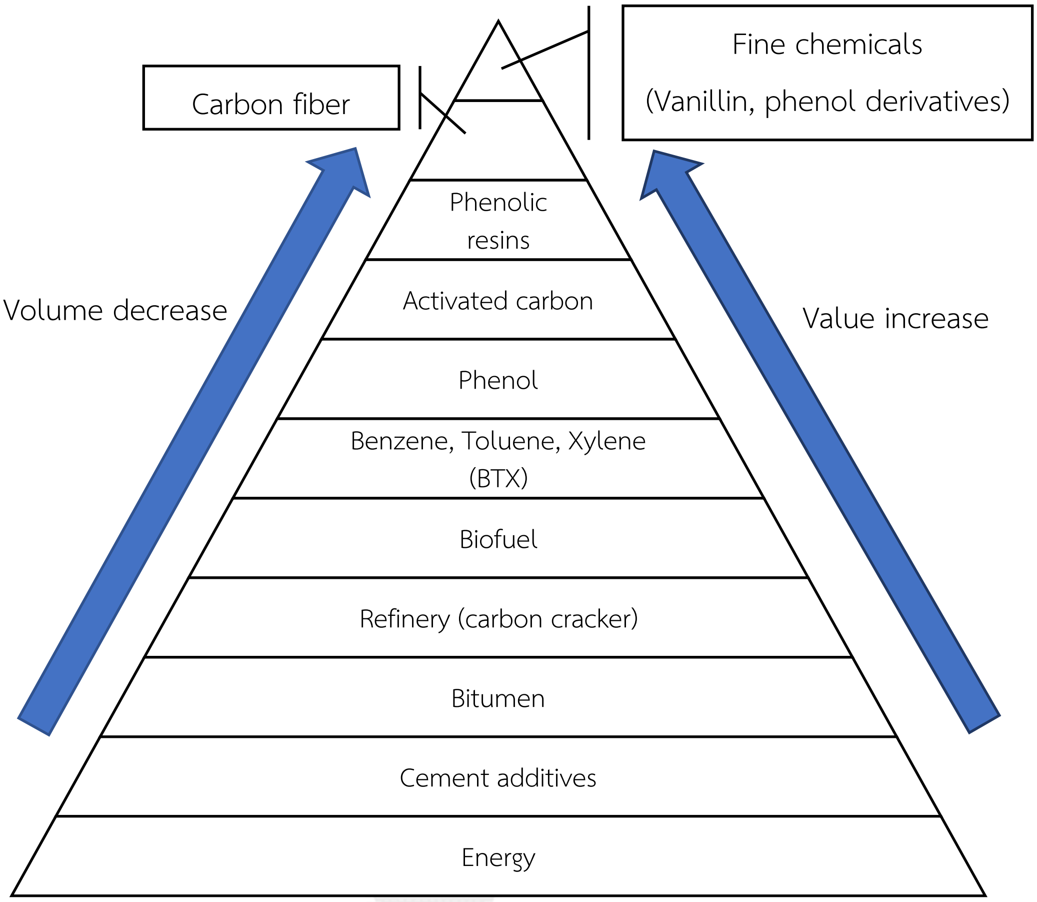


Figure 2-6 Products from Kraft lignin [9]

Because Kraft lignin is the big network of aromatic component, it can be changed to many valuable aromatic products as shown in Figure 2-6. This thesis concentrates on vanillin product that is located at the top of this figure because it has the highest value and is needed widely in food industry. Natural vanillin supply is not enough to meet to market demand and so synthetic vanillin production is essentially needed. However, the main problem of synthesis vanillin production is that the yield of vanillin that can be obtained from existing processes is not much. So, the study to find the optimal process condition that gives the highest vanillin yield is the topic of this thesis.

2.3 Vanillin

Vanillin is phenolic compound which has structure as shown in Figure 1-1. Today, synthetic vanillin is used more often than natural vanillin. This is because the natural vanillin is very expensive if compared with synthetic vanillin. Price of natural vanillin is around 2,000-4,000 $/kg [10] but price of synthesis vanillin is around 15-1,000 $/kg [10]. The current global demand of vanillin is estimated to be around 20,000 tons per year [4]. Nowadays, the main pathways to produce synthetic vanillin are petroleum-based pathway and lignin-based pathway.

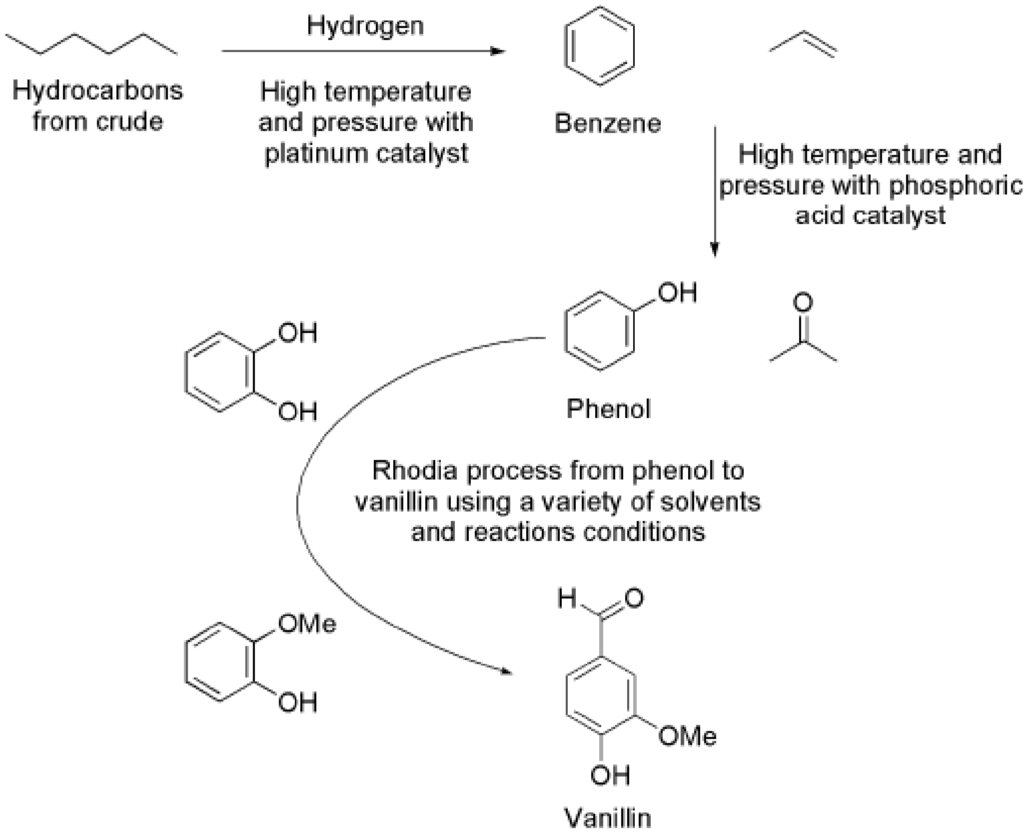


Figure 2-7 Vanillin from crude oil [10]

2.3.1 Vanillin synthesis method

From Figure 2-7, the most popular method of synthetic vanillin production on today is the petroleum based pathway. It starts with cracking of large molecule of hydrocarbons from crude and remove hydrogen in the molecule to get benzene. A Rhodia process was developed by Rhodia Company since the 1970s. This process starts with changing benzene that is obtained from dehydrogenation of crude to phenol by hydroxylation using hydrogen peroxide. After that, catechol is changed to guaiacol by methylation reaction. The main reaction to produce vanillin from guaiacol has two important steps. In the first step, guaiacol reacts with glyoxylic acid by electrophilic aromatic substitution to produce vanillylmandelic acid. The second step is conversion of vanillylmandelic acid to vanillin by oxidative decarboxylation.

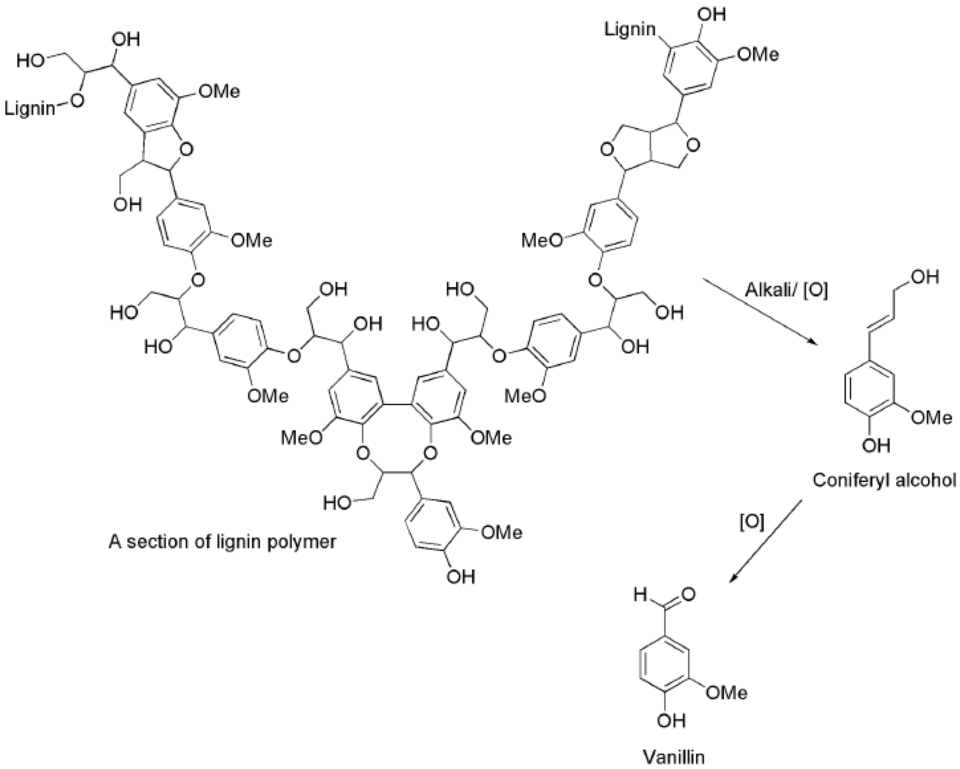


Figure 2-8 Vanillin from lignin [10]

This thesis focuses on lignin-based pathway that is one of bio-based pathway because lignin is a main component in wood. There are several methods that can change Kraft lignin to vanillin. The most popular method is direct oxidation of Kraft lignin to produce vanillin. This is because direct oxidation process is a simple process and the reaction time is short. Other pathway that can also produce vanillin from Kraft lignin is pyrolysis. However, it operates at much higher temperature and the reaction is much more complex. So, it is more difficult to set up experiment and control the process.

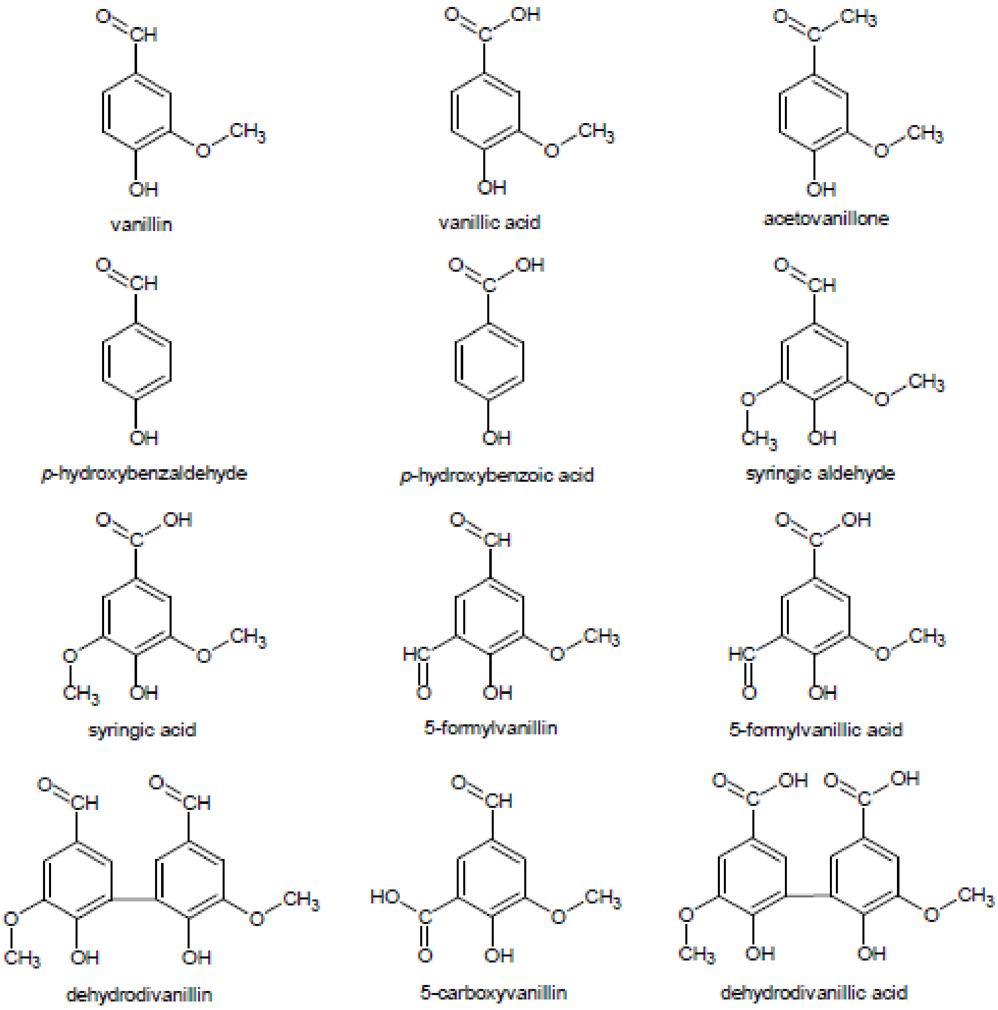


Figure 2-9 Lignin oxidation products [11]

The main reaction of lignin oxidation in alkaline solution is alkyl aryl ether hydrolysis (depolymerization) to small molecule and some molecule continue to react with oxygen in solution and transform to vanillin as shown in Figure 2-8. All products of lignin oxidation are showed in Figure 2-9 as above.

Fargues et al. [6] studied the kinetic models for simulation of Kraft lignin oxidation in batch reactor by setting up experiment and use oxygen to be the oxidant at reaction temperature of 110-154 ^{0}C, oxygen partial pressure of 1.2-5 bar and initial Kraft lignin concentration of 30-120 g/l. They found that the maximum vanillin yield was 10% at a reaction temperature of 130 ^{0}C, an oxygen partial pressure of 3 bar, a total pressure of 9 bar, and an initial lignin concentration of 60 g/l in an alkaline medium of 2 N NaOH. The kinetic model of lignin oxidation in a batch reactor consisted of two main reactions. The first reaction is degradation of lignin to vanillin and the other reaction is vanillin degradation to other compounds as summarized in equation (1)

$$\alpha L \overset{r_1}{\rightarrow} V \overset{r_2}{\rightarrow} DC \tag{1}$$

α = stoichiometry of reaction 1 as calculated by

$$\alpha = \frac{M_v}{0.13M_n} \tag{2}$$

where

M_v = Molecular weight of vanillin

M_n = Molecular weight of lignin

The reaction rate of lignin oxidation (reaction 1) for isothermal system is discussed as below. For isothermal system, the reaction rate is studied based on constant liquid and gas volume. Hence, the reaction rate and mass balance of this system are defined by concentration number [11]. The reaction rate of lignin oxidation to vanillin (reaction 1) was reported in equation (3)

$$r_1 = k_1 {C_{O_2}}^{1.75} C_L \tag{3}$$

Lignin oxidation reaction rate was related with oxygen concentration (C_{O_2}) by power 1.75 and lignin concentration (C_L) by power 1.

Mathias [12] calculated and reported the reaction constant of reaction 1 (k_1) by

$$k_1 = k_1^0 \exp(-\frac{E_a}{RT}) \tag{4}$$

where

k^0_1 = 1.376X10^7 (l/mol)$^{1.75}$min^{-1}

The reaction rate of vanillin oxidation (reaction 2) was studied. The reaction rate was found to be dependent on pH value in reaction as followed.

If pH≥11.5

$$r_2 = k_2 C_{O_2} C_V \tag{5}$$

$$k_2 = 4.356 \times 10^6 exp\left(-\frac{5530}{T}\right) \tag{6}$$

He also reported the concentration of dissolved oxygen (C_{O_2}) by

$$C_{O_2} = \left(3.559 - 6.659 \times 10^{-3}T - 5.606\, P_{O_2} + 1.594 \times 10^{-5} P_{O_2} T^2 + 1.498 \times 10^3 \frac{P_{O_2}}{T}\right) \times 10^{-3} \times 10^{-0.144I} \tag{7}$$

If pH<11.5

$$r_2 = Af(pH)C_V^2 \tag{8}$$

where

$$A = 4071 exp\left(-\frac{3103.7}{T}\right) \tag{9}$$

$$f(pH) = \left(\frac{BC_{H+}}{1+BC_{H+}}\right)^2 \tag{10}$$

$$B = 8.88\, X\, 10^{12}\, exp\,(-\frac{1936.6}{T}) \tag{11}$$

$$C_{H+} = 10^{-pH} \tag{12}$$

The pH value can be estimated by *X* value which is the factor that shows all possible acid products from lignin oxidation as shown in eq. (13)

$$X = 0.03774\ M_n\ (C_{Li}\text{-}C_L) \tag{13}$$

If X < 1N

$$pH = 14 \tag{14}$$

If 1N< X < 1.9955N

$$pH = 14 + \log_{10}(2 - X) \tag{15}$$

If 1.9955N< X < 2N

$$pH = pK_a + \log_{10}\left[\frac{X}{\left(\frac{K_w X}{K_a}\right)^{1/2}} - 1\right] \tag{16}$$

where

pK_a = 9

K_a = 10^{-pKa}

If X>2N

$$pH = pK_a + \log_{10}\left(\frac{2}{X-2}\right) \tag{17}$$

The material balances of each species in reaction are shown in equation (18), (19) and (20).

Lignin

$$\frac{dC_L}{dt} = -\alpha\, r_1 \tag{18}$$

Vanillin

$$\frac{dC_V}{dt} = r_1 - r_2 \tag{19}$$

Vanillic acid

$$\frac{dC_D}{dt} = r_2 \tag{20}$$

Where

C_L = Kraft lignin concentration

C_V = Vanillin concentration

C_D = Vanillic acid concentration

Araújo [11] studied further on mathematic models of the Kraft lignin oxidation resulted from the study of Fagues et al. [6]. They created mathematic models and compared the result with experimental data of Mathias [12]. They found that these models are accurate to simulate Kraft lignin oxidation in batch reactor. In 2010, they studied about the effect of Kraft lignin sources to vanillin concentration in products stream by comparing vanillin concentration produced from two sources of Kraft lignin that have molecular weight of 1141 and 2325 g/mol. They found that Kraft lignin source that has lower molecular weight gave better vanillin yield.

Table 2-1 Vanillin yield obtained from lignin oxidation [13]

Lignin type	Oxidant	Feed lignin (g/l)	T (^{0}C)	P_{O2} (bar)	Time (min)	%Vanillin yield	Ref.
Pinus spp. Westvaco	O_2	60	141	3.8	64.4	10.5	Mathias [12]
Pinus pinaster Portucel	O_2	82.5	127	3.5	92.9	4.1	Mathias [12]
Black liquor Portucel	O_2	50	119	3.5	77.5	8.0	Mathias [12]
Indulin AT Westvaco	O_2	60	123	4.0	75.0	3.7	Araújo [11]
Pinus spp.	Nitro-benzene	60	147	-	420	13.0	Mathias et al. [14]

The results from some literatures that studied about direct lignin oxidation with various oxidants are concluded in Table 2-1. From the table, the maximum vanillin yield that could be obtained from lignin oxidation is 13%w/w from reaction that used nitrobenzene as oxidant at 7h of reaction, 147 °C, 2N NaOH and 0.84 mL of nitrobenzene per gram of initial lignin. For lignin oxidation by oxygen, the maximum vanillin yield is around 10.8% w/w from oxidation reaction at 133 °C, oxygen partial pressure of 2.8 bar, initial lignin concentration of 60 g/l dissolved in 2N NaOH at 35 minutes of reaction.

Borges da Silva et al. [13] studied about the integrated process to produce vanillin and lignin based polyurethanes from Kraft lignin. They experimentally studied Kraft lignin oxidation in alkaline medium in two types of reactor which are structured packed bubble column reactor (SPBCR) and bubble column reactor (BCR). They found that the SPBCR reactor gave better vanillin yield than the BCR reactor. However, the resultant yield was still lower than that of a batch reactor.

Rodrigues Pinto et al. [15] studied about the yield of vanillin that was obtained from oxidation with oxygen in alkaline medium from different lignin sources. Those sources are industrial Eucalyptus globulus sulfite liquor and Kraft liquors that were collected from different steps before entering the recovery boiler. There are direct oxidation of pulping liquor and oxidation of Kraft lignin isolated from liquor. They found that oxidation of isolated Kraft lignin gave 28 kg of syringaldehyde and 12 kg of vanillin per ton of Kraft lignin. This result was slightly lower than sulfite liquor. They also found that the Kraft lignin had advantage for selectivity as indicated by aldehyde/ acid ratio.

2.3.2 Vanillin separation process

The separation of vanillin from products stream produced from reactor can be achieved by several methods. Each method gives difference purity of synthesis vanillin. For industrial scale, some pulping production company in Canada uses liquid-liquid extraction technique with suitable solvents such as benzene and toluene after acidification to precipitate high molecular weight molecule in medium. But this method uses high amount of solvents and some vanillin in solution will be lost during acidification step because vanillin will be co-precipitated in this step [13].

The first development of solvent extraction technique is done by changing solvent from organic solvent such as benzene and toluene to supercritical CO_2 [16]. The supercritical CO_2 is inorganic solvent that is non-toxic and gives less effect to environment. However, this process operates at very high pressure. So, this method uses very high energy and results in high operating cost.

Other method that can be used to extract vanillin from the mixed products stream is adsorption by Zeolite and macroporous resin absorbents [17,18].

Both mentioned methods require acidification step prior to vanillin exaction process in order to remove lignin from solution. And the main problem of both methods is that they require very large amount of acid. To reduce this amount, another method that directly isolate molecular of phenolates from mixture before performing acidification was proposed. This method can reduce large amount of acid. One of isolating method is elution of products stream from oxidation reaction on a strong cation-exchange resin in the Na^+ form. [19]

Borges da Silva et al. [13] proposed a separation method of vanillin from products stream of Kraft lignin oxidation as follows.

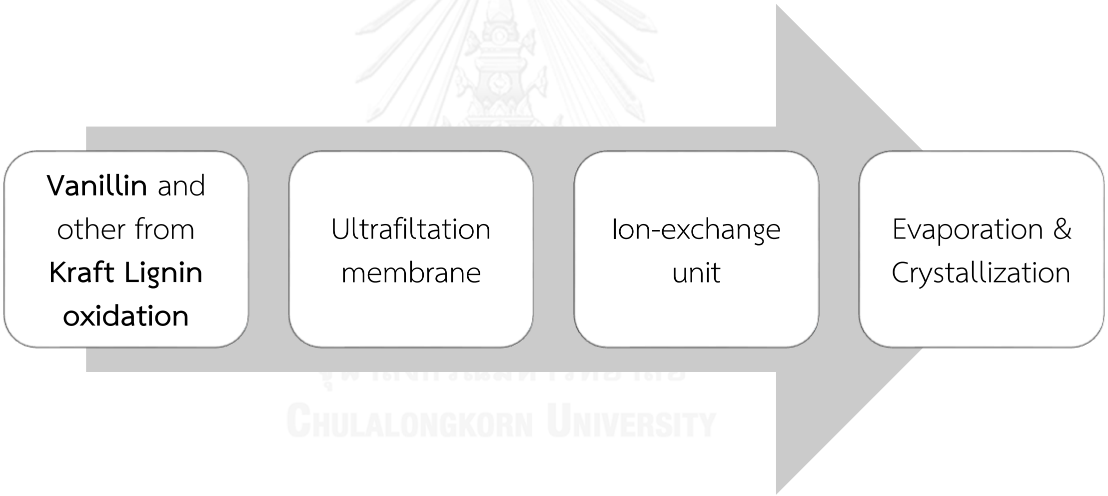


Figure 2-10 Vanillin separation process

From Figure 2-10, vanillin and other oxidation products are sent to separation process. The first step of separation is ultrafiltration (UF). This is done by feeding product steam to ultrafiltration membrane. Vanillin and vanillin related species that have lower molecular weight are separated to permeate stream while the remaining lignin is retained in retentate stream. The retentate stream is sent back to feed tank for reuse as raw material and the permeate steam is sent to ion-exchange unit. Vanillin leaving from oxidation process is in sodium form because of the use of excessive amount of sodium hydroxide in reaction. H^+ ion from resin exchanges with Na^+ in solution to produce vanillin and resin is converted to sodium form. Vanillin and impurities from oxidation reaction that contain vanillin acid, 5-formyl vanillin, o-vanillin and acetovanillone are purified by being dissolved in solvent mixture of water and methanol. Then, it is sent to crystallization step. Here, the mixture solution is stirred and cooled down to 5 ^{0}C and then the crystallized mixture goes to filtration step. After that, the filter cake is washed by water at 5 ^{0}C and is evaporated to remove water. If vanillin purity is still not achieved, one more crystallization step may be added to purify vanillin.

Other possible method is extraction followed by distillation. Sandborn [20] proposed a method to separate vanillin by using extraction with suitable solvent followed by distillation to remove the spent solvent.

Werhan [21] proposed a conceptual process for the catalytic oxidation of Kraft lignin to get monomeric products. The proposed process contain three main parts i.e. process reaction, product separation and purification. For the reaction part, this work focused on acidic oxidation of Kraft lignin in methanol/water solution so, products of this reaction consist of vanillin and many impurities in methyl form. Those impurities comprise methyl vanillate, methyl dehydroabietate, 5-carbomethoxy-vanillin and methyl 5-carbomethoxy-vanillate. The separation and purification process in this work were carried out by removing methanol using flash separation followed by solvent extraction with ethyl acetate to recovery monomeric products from products stream. After that most ethyl acetate was recovered from products stream by solvent nanofiltration membrane. The remaining ethyl acetate in products stream was removed by solvent recovery unit. Then, the mixture of monomeric products was separated by vacuum distillation followed by crystallization to remove vanillin and methyl vanillate and finally followed by supercritical CO_2 extraction to remove the remaining impurities. This method offered complete purification of vanillin and impurities. So, it will get additional revenue from selling of impurities.

2.4 Separation method theory

2.4.1 Liquid-Liquid extraction

Liquid-Liquid extraction or solvent extraction is a separation method that is operated based on different relative solubility of solute in two immiscible liquids.

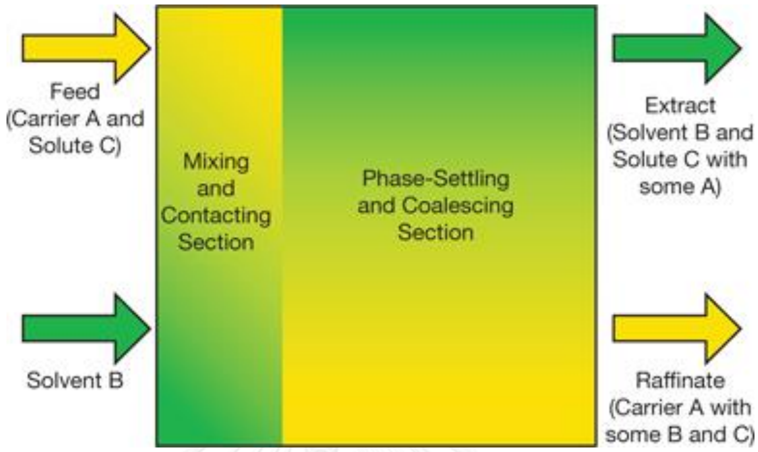


Figure 2-11 The extraction unit simulation [22]

From Figure 2-11, a carrier liquid (carrier A) contain component (to be extracted) or solute C feed to extraction unit. In this unit, the carrier liquid will contact with solvent feed (solvent B) that these two liquid must be immiscible or only slightly miscible. The solute C in carrier liquid can dissolve in solvent stream better than the carrier stream. As a result, the mass transfer of solute C from the carrier liquid to solvent stream will occur. The exit streams from the extraction unit contain extract stream (solvent B and solute C with some carrier A) and raffinate stream (carrier A with some B and C).

The suitable solvent for solvent extraction to separate vanillin and monomeric compound from Kraft lignin oxidation products must have following properties [21]

- High solubility in monomeric products but immiscible or only slightly miscible in reaction solvent.
- Density has sufficient difference with density of reaction solvent for phase separation.
- Nonreactive to other component in reaction products stream.

- Easy to recovery and low volatility.
- High thermal changing resistant.
- Low toxic and environment impact.
- Lost cost.

From above properties, there are 5 suitable solvents [21] that have been theoretically studied with Aspen Plus® and reported in the literature. They are chloroform, toluene, hexane, diethyl ether and ethyl acetate.

Shakeel et al. [23] also studies about the solubility of vanillin in ten different environmentally benign solvents. That ten solvents are water, ethanol, ethylene glycol (EG), ethyl acetate (EA), isopropanol (IPA), propylene glycol (PG), polyethylene glycol-400 (PEG-400), Transcutol, butanol-1 and butanol-2. The studied temperature range of this work was 298–318 K. They found that the highest mole faction of vanillin solubility is achieved by PEG-400 ($4.29 \text{ X}10^{-1}$ at 298 K) followed by Transcutol, EA, butanol-2, ethanol, EG, PG, IPA, butanol-1 and water and the solubility of vanillin will increase if temperature increases. This report can be used as a guideline to select the suitable solvent for vanillin separation from Kraft lignin oxidation products stream.

From the study of Shakeel et al. [23], ethyl acetate was found to be the most suitable solvent for vanillin separation from Kraft lignin oxidation products, among the five solvents studied. This is simply because vanillin solubility in ethyl acetate is higher than other commercial solvent (except PEG-400 and Transcutol). In addition, ethyl acetate is less toxic than chloroform, toluene, and hexane.

Diddams et al. [24] reported about the preferably process condition of vanillin extraction from aqueous crude mixture products from lignin oxidation. They reported that the extraction temperature could be carried out at above 30 ^{0}C. The preferably temperature range is 60-100 ^{0}C and the most preferably extraction temperature is 70 ^{0}C. If the temperature is higher that this preferably range, the extracted solvent will become less selectivity. The preferable amount of vanillin in mixture for solvent extraction is in a range of 5-25%. And the best vanillin amount that could get a good selectivity for solvent extraction is found at 20%.

2.4.2 Crystallization

Crystallization process is a solid-liquid separation method. This method is used to separate solids that are dissolved in liquid. Normally, crystallization is used as a final separation step for vanillin and other food or drug production process. This is because this method can give high purity of final product. In case of vanillin, the specification of food grade vanillin purity must exceed 99.8% [13] so, crystallization is the suitable final separation unit. The principle of crystallization process is based on solubility of compound in solvent, which could be altered by adjusting some process condition such as temperature, pressure, pH etc. Under appropriate conditions, solubility of a compound will be decreased and the compound will become indissoluble and form a crystalline solid. The crystallization process contains two main fundamental steps. They are nucleation and crystal growth step. The nucleation step is where the solute or compound dissolves in solvent. Then, it starts to gather into cluster and becomes stable in present process condition. This stable cluster forms the nuclei. Then, the nucleuses will growth into a macro size in crystal growth step. The driving force of crystallization process is concentration difference [25].

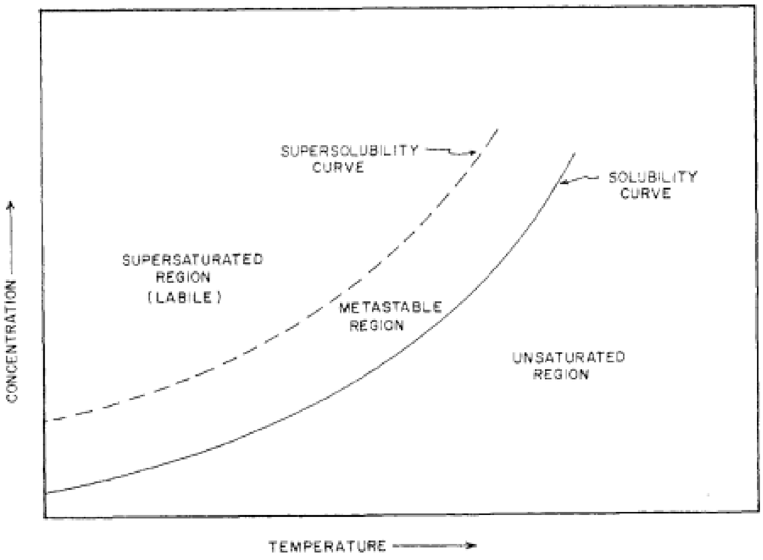


Figure 2-12 Typical super solubility diagram [25]

According to diagram in Figure 2-12, this is typical super solubility diagram. This diagram has three regions which are unsaturated region, metastable region, and supersaturated or labile region. In the unsaturated region, the nucleation and crystal growth cannot occur. The existing crystal still dissolves in solution. When temperature cool down to metastable region, the existing crystal will growth but no new crystal are formed. When cooling until the temperature reaches supersaturated region, the spontaneous formation of new crystal will occur.

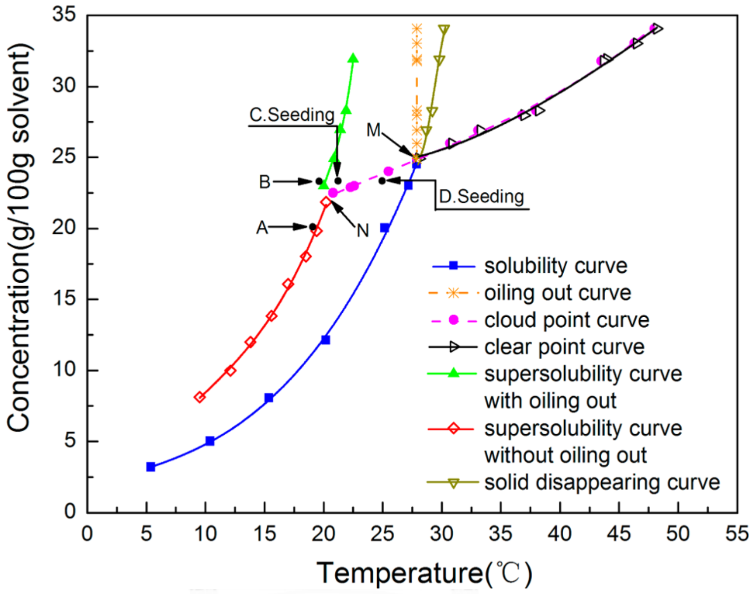


Figure 2-13 Phase diagram of vanillin in 20 wt % 1-propanol/water mixture [26]

Zhao et al. [26] studied about the crystallization process of vanillin in 1-propanol/water solvent. They reported a phase diagram as illustrated in Figure 2-13. The diagram shows the solubility data of vanillin in 20%wt 1-propanol/water mixture. This diagram can be used to design the suitable crystallization process condition. The crystallization could be obtained to avoid the oiling out that it can affect to the vanillin purity after crystallization. From the diagram, the supersolubility curve without oiling out is red line so, the suitable crystallization temperature is lower than 20.5 ^{0}C and concentration of vanillin in solution is lower than 22.5 g/100 g of solvent.

2.5 Techno-economic analysis

Techno-economic modeling is a method to study and find the most appropriate operating conditions that give the best profit by using product yield and energy consumption as decision parameter.

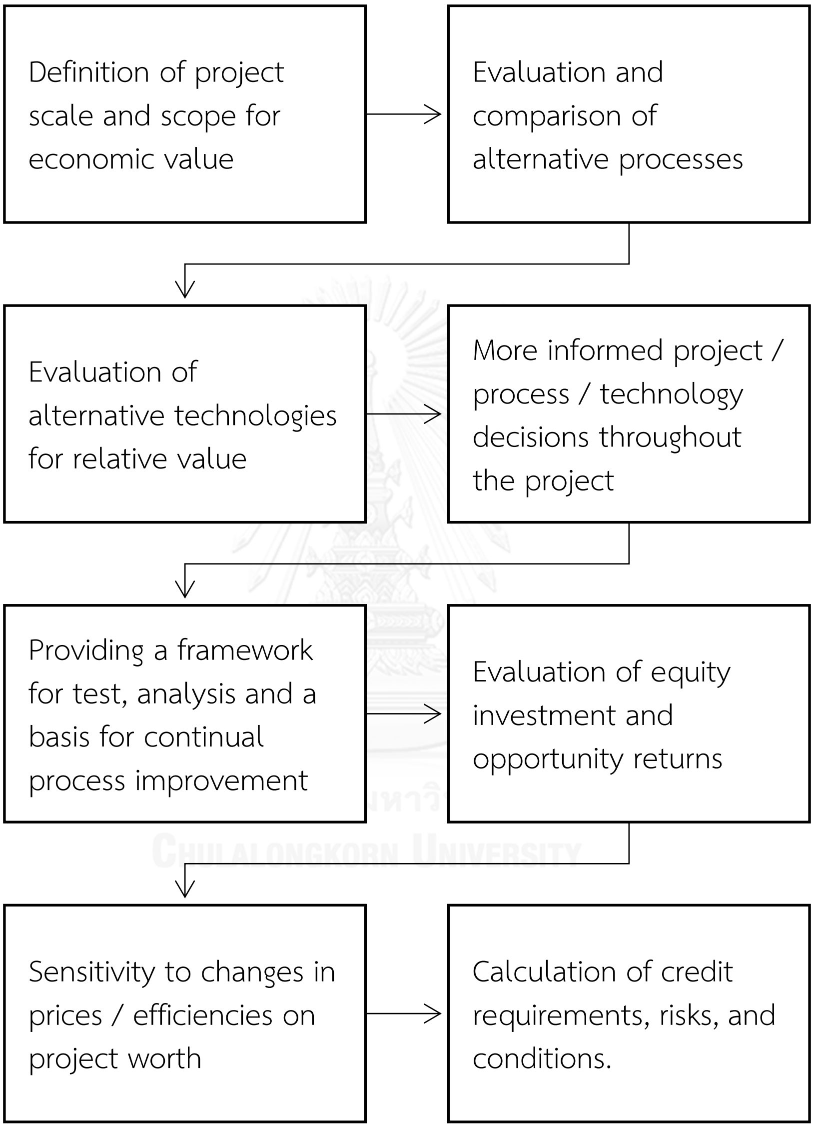


Figure 2-14 Process of techno-economic analysis [27]

This model can help reduce the unnecessary cost and investment risk. The procedure of this modeling is shown in Figure 2-14.

Measfun et al. [28] studied about techno-economic assessment of integration of the organics extraction process for producing high grade lignin with the Kraft pulping process and the integration of organic extraction and conventional ABE process with Kraft pulping process. They studied the cost of each integration process by using equation as illustrated below.

$$Capital\ cost = \sum\left[(Equipment\ purchase\ cost \times h_f \times f_m)\right] \times f_i \times f_b \times f_p \qquad (21)$$

where

h_f = Hand factor

f_m = Material factor

f_i = Instrument factor

f_b = Building factor

f_p = Place factor

They searched the equipment purchase costs from literatures, Engineering Economics and Economic Design for Process Engineers book and used all factors from chemical engineering plant cost index (CEPCI). They found that integrating only lignin separation process with Kraft pulping production was an effective solution to increased pulp production capacity and incomes.

Benali et al. [29] studied about the integration of lignin-based biorefinery from Canadian softwood Kraft pulp mill by considering the extra consumption on resources included steam, water, carbon dioxide and sulfuric acid of integrating lignin separation in Kraft pulp mill. They also studied about economic viability assessment that was carried out toward four scenarios. The first and second scenarios are reference cases relating to only Kraft pulp mill without a pulp production increase but with/without advance process integration of lignin separation. The third and fourth scenarios are the study cases to integrate lignin separation process with a pulp production increase by 5, 10, and 15%. They found that integrating Kraft lignin separation from black liquor and combining with increased pulp production process is a cost-effective scheme to operate. The maximum lignin separation from Kraft pulp mill process was 50 tonne per day assuming pulp production capacity of 400 tonne per day. This integrated process could reduce energy load by up to 14.1 MW and reduce water consumption by up to 1.9 million-m^3/year. The separation of Kraft lignin of 50 tonne/day could give additional revenues of up to 12.5$ millions/year with a payback period less than 2 years.

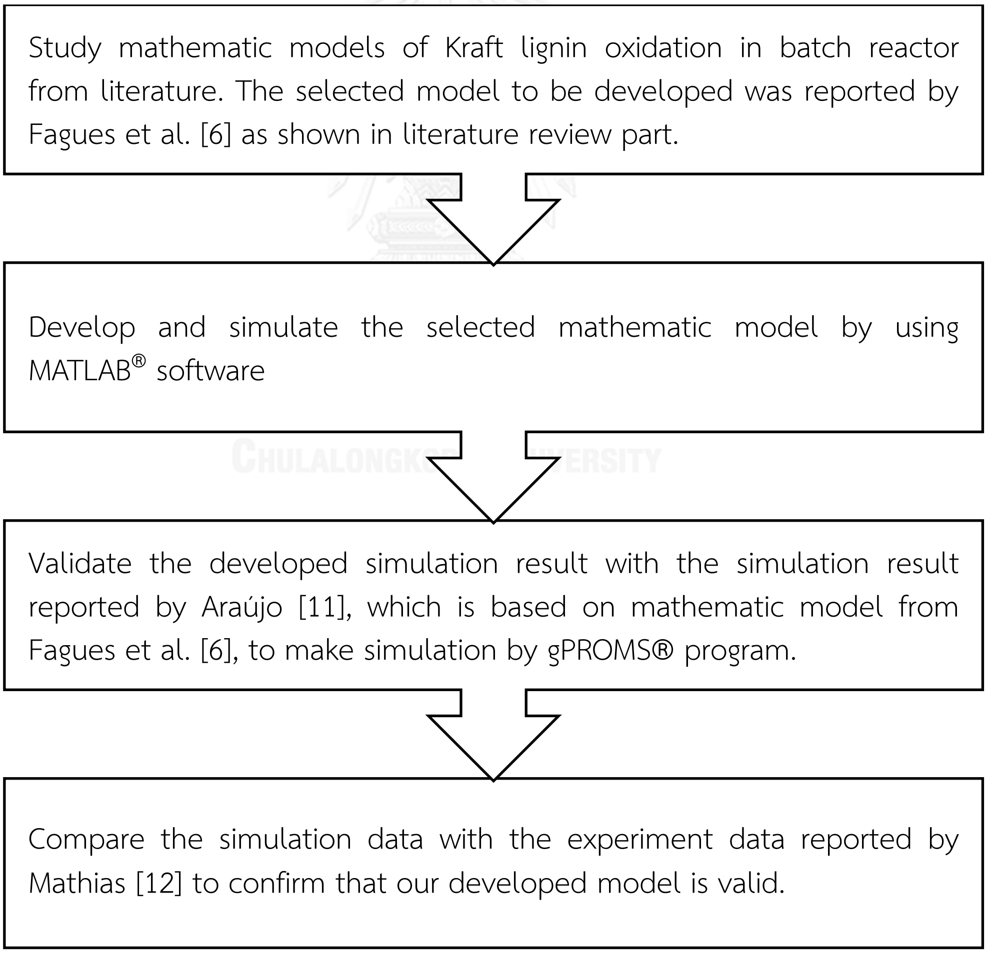
CHAPTER III

RESEARCH METHODOLOGY

The research methodology is divided into 4 parts. They are setting up based simulation model, finding optimal process condition, simulation of vanillin production process by Aspen Plus$^{®}$ software, and techno economic analysis.

3.1 Setting up based simulation model

The method for setting based simulation model of Kraft lignin oxidation is shown as below diagram.



Study mathematic models of Kraft lignin oxidation in batch reactor from literature. The selected model to be developed was reported by Fagues et al. [6] as shown in literature review part.

Develop and simulate the selected mathematic model by using MATLAB$^{®}$ software

Validate the developed simulation result with the simulation result reported by Araújo [11], which is based on mathematic model from Fagues et al. [6], to make simulation by gPROMS® program.

Compare the simulation data with the experiment data reported by Mathias [12] to confirm that our developed model is valid.

For MATLAB$^{®}$ program, the selected solver used to solve ODE problems is ODE45 solver. This is because ODE45 performs well with most ODE problems and thus it should generally be the first choice following MATLAB® program's recommendation. It should be noted ODE15 solver has also been tested and the result was no different from the result of ODE45.

3.2 Finding optimal process conditions

After a valid mathematic model of Kraft lignin oxidation in batch reactor is obtained, the next step is to optimize the process parameters in order to maximize the vanillin yield. The process parameters that were studied in this work are as follows:

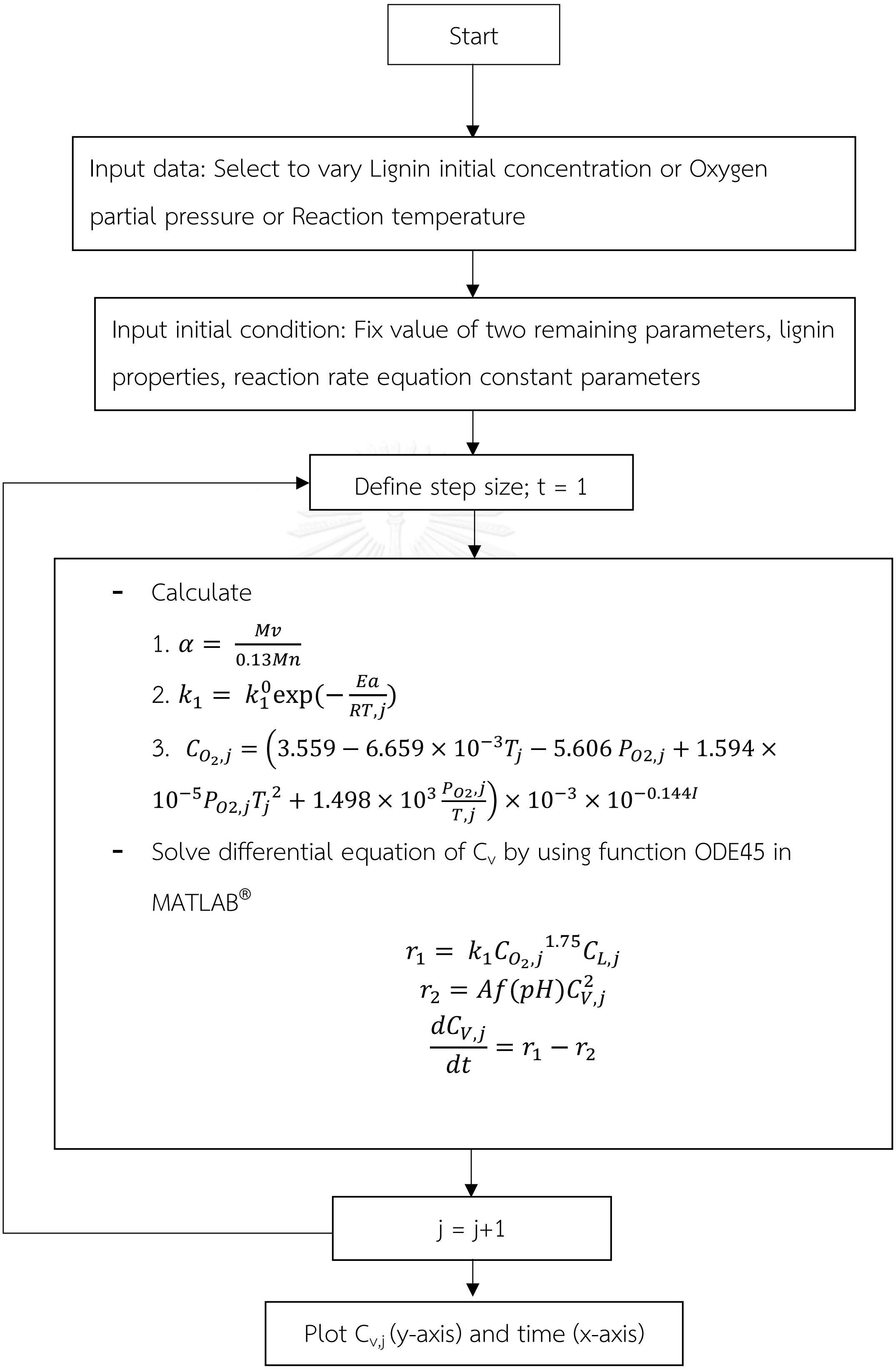
- ○ Oxygen partial pressure
- ○ Initial lignin concentration
- ○ Reaction temperature

Table 3-1 Process parameters in this work

Process parameters	Value	Ref.
Molecular weight of Kraft lignin (MW)	1141	Mathias [12]
Ea/R (reaction 1)	3502	Mathias [12]
Feed oxygen partial pressure (bar)	1-5	Fargues et al. [6]
Initial concentration of Kraft lignin (g/l)	30-120 (limit of model)	Araújo [11]
Reaction temperature (^{0}C)	110-154	Fargues et al. [6]

The process parameters and their operating range used for simulation in this work are showed in Table 3-1.

The simulation result obtained from the Kraft lignin oxidation with optimal process condition will be validated with experiment data reported by Mathias [12], to make sure that our optimized condition aligns with the experiment data. The computational diagram of simulation steps to find the optimal process conditions is showed in Figure 3-1.



Input data: Select to vary Lignin initial concentration or Oxygen partial pressure or Reaction temperature

Input initial condition: Fix value of two remaining parameters, lignin properties, reaction rate equation constant parameters

Define step size; t = 1

- Calculate

1. $\alpha = \frac{Mv}{0.13Mn}$

2. $k_1 = k_1^0 \exp(-\frac{Ea}{RT,j})$

3. $C_{O_2,j} = \left(3.559 - 6.659 \times 10^{-3} T_j - 5.606\, P_{O2,j} + 1.594 \times 10^{-5} P_{O2,j} {T_j}^2 + 1.498 \times 10^3 \frac{P_{O2,j}}{T,j}\right) \times 10^{-3} \times 10^{-0.144I}$

- Solve differential equation of C_v by using function ODE45 in MATLAB®

$$r_1 = k_1 {C_{O_2,j}}^{1.75} C_{L,j}$$

$$r_2 = Af(pH) C_{V,j}^2$$

$$\frac{dC_{V,j}}{dt} = r_1 - r_2$$

j = j+1

Plot $C_{v,j}$ (y-axis) and time (x-axis)

Figure 3-1 Computational diagram of simulation process

3.3 Simulation of Vanillin production process by Aspen Plus® software

In this step, the process conditions obtained from the MATLAB® simulation and information from literatures are integrated and used to design a Kraft lignin oxidation process by using ASPEN Plus® software. Once a complete process flowsheet of the Kraft lignin oxidation process is obtained, we can determine all necessary process equipments and energy consumption of the process.

Table 3-2 Ultimate and Proximate analysis of Kraft lignin (dry sample) for simulation in this work [30]

Ultimate analysis	wt%	Proximate analysis	wt%
C	64.36	Fixed carbon	39.88
H	5.88	Volatile matter	58.17
N	0.65	Ash content	1.95
O	27.65		
S	1.46		

The properties of Kraft lignin used for the simulation in Aspen Plus® are shown in Table 3-2 and the process description is described in the next section.

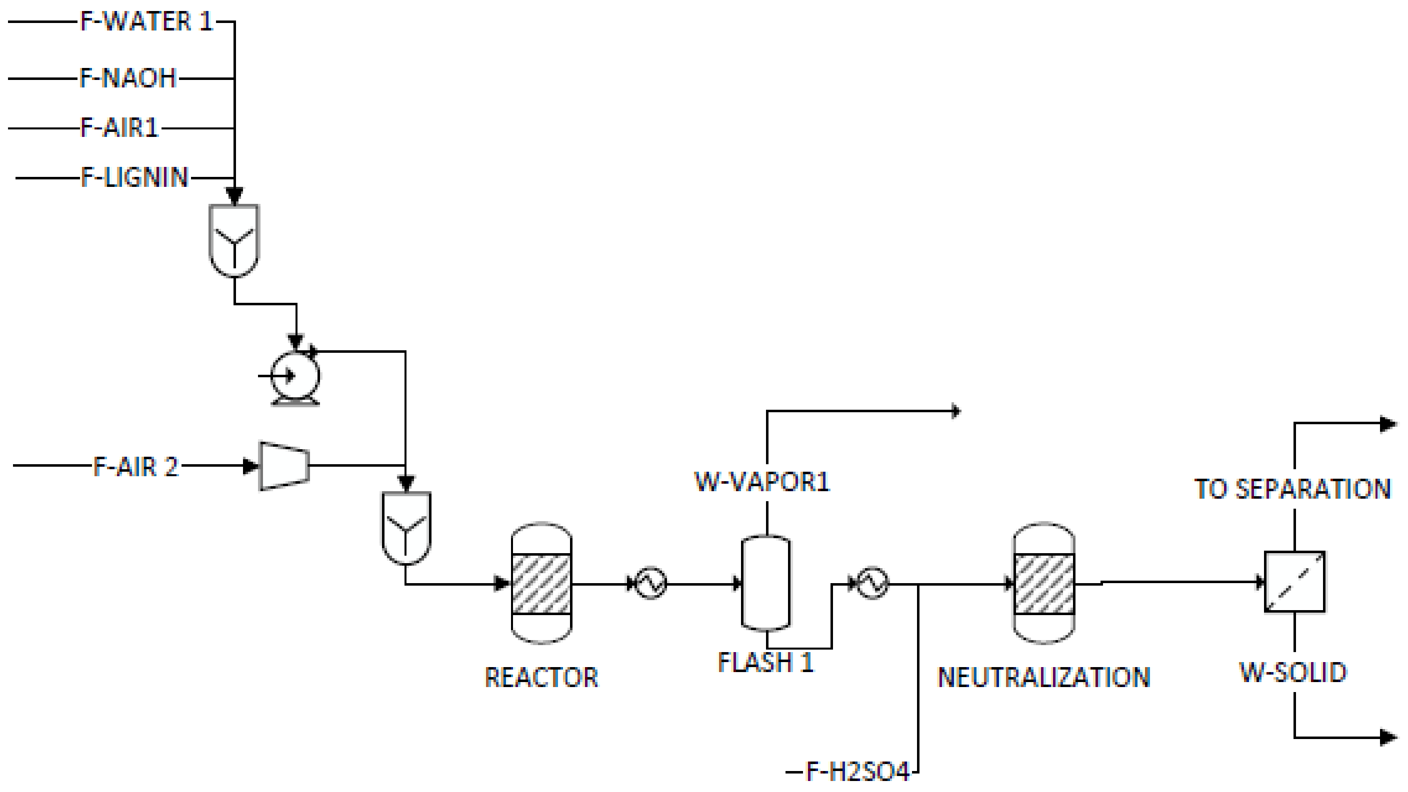


Figure 3-2 Block flow diagram of vanillin production process from Kraft lignin

3.3.1 Lignin oxidation process

A block flow diagram of lignin oxidation process to produce vanillin is shown in Figure 3-2. First of all, lignin together with oxygen feed from air, sodium hydroxide and water are mixed together and fed to pump. This pump increases pressure of solution from atmospheric pressure to 10 bar. The remaining required oxygen is supplied by air compressor and mixed with the solution. The mixed solution is then fed to oxidation reactor. The oxidation reaction takes place inside the reactor and partial lignin is converted to vanillin and related products.

Table 3-3 Reaction parameters used to simulate in oxidation reactor unit

Parameters	Value	Ref
Feed components		
Kraft Lignin (kg/hr)	Set up	Set up to produce vanillin 100 kg/hr
Oxygen (kg/hr)	Mass balance	Appendix A
Water (kg/hr)	Full fill solution	Araújo [11]
NaOH (kg/hr)	1.33XFeed lignin	Araújo [11]
Process condition		
Reaction temperature	110 ^{0}C (The best condition from section 3.2)	
Oxygen partial pressure	5 bar (The best condition from section 3.2)	
Total pressure	10 bar	Araújo [11]

The operation conditions of this reactor is shown in Table 3-3. Products from oxidation reactor including the remaining raw materials are cooled down to 102 ^{0}C before sending to a flash tank. The flash tank is used to reduce pressure of products solution from 10 bar to 1 bar and remove some of water contained in the product stream. The reaction products including remaining lignin go are further cooled down to 80 °C and sent to neutralization tank for precipitation of the remaining lignin. The oxidation products are neutralized with sulfuric acid to reduce pH of products solution from pH 14 to pH 7. Lignin that is dissolved in strong base solution will coagulate when pH of solution is decreased to neutral. The remaining lignin in solid form is separated from products solution by a solid filter.

Because the products produced from lignin oxidation reaction contain many impurities. It is important to study and design a suitable vanillin separation and purification process to meet the product specification of vanillin, which is vanillin purity of 99.5%.

To determine the suitable vanillin separation process, we performed process design and simulation to investigate and compared three different separation pathways. The best separation pathway will be considered and selected based on the results of energy consumption requirement and economics viability of the process. Also, a conventional separation process used in vanillin production from petrochemical feedstock is simulated and compared with the three different proposed separation processes. Their details are provided in the next sections.

All simulation pathway is designed to produce vanillin product amount 100 kg/hr.

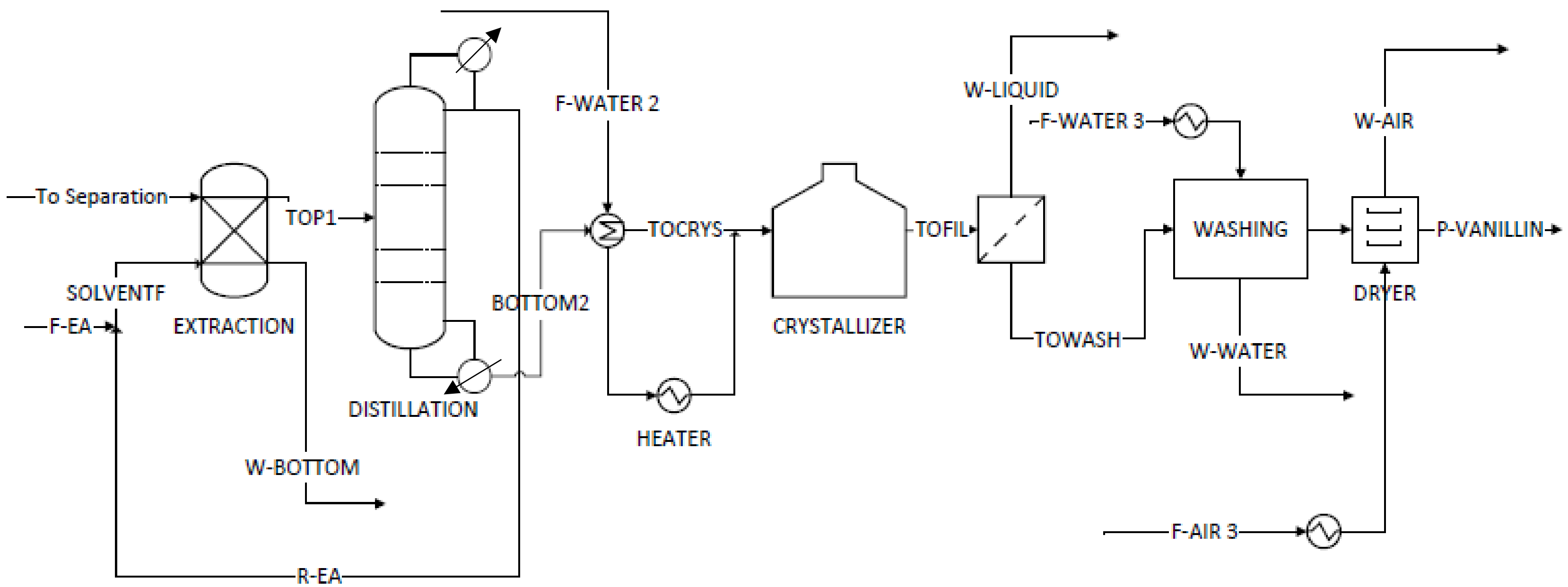


Figure 3-3 Block flow diagram of vanillin separation process pathway 1

3.3.2 Products separation process pathway 1

The first separation pathway is shown in Figure 3-3. After neutralization, the oxidation products solution is fed at top of extraction column while extraction solvent is fed at bottom of the column. Vanillin and other phenolic compounds are extracted from the solution. It should be noted that the main impurity in the solution is sodium sulfate resulted from neutralization in the previous step. The extract containing vanillin and other phenolic compounds goes to a distillation column to separate the solvent from vanillin products. The recovered solvent in distillate stream is then recycled to extraction column for reuse again.

Table 3-4 Process conditions for extraction column in separation process pathway 1

Parameters	Value
Extraction column stages	10
Ethyl acetate (kg/hr)	531
Pressure (bar)	1
Temperature (^{0}C)	80

Table 3-5 Process conditions of distillation column in separation process pathway 1

Parameters	Value
Distillation column stages	10
Distillate rate (kg/hr)	90
Reflux ratio	10
Pressure (bar)	1

The process conditions of extraction column and distillation column are show in Table 3-4 and Table 3-5 respectively.

Table 3-6 The solubility of vanillin in water data for crystallization process [31]

T (°C)	**Solubility (g/l)**
20	12.86
40	25.43
60	38.57
80	50.00
100	62.86

The next step is crystallization process to separate vanillin from other phenolic compounds. This process uses the difference in solubility in crystallization solvent (water for this pathway) of vanillin and other phenolic compounds to purify vanillin product. The solubility of vanillin in water is shown in Table 3-6. Water is fed to crystallizer to make a saturated solution before crystallizing. The crystallizing temperature is 5 °C at atmospheric pressure. Vanillin crystal obtained from crystallizer is separated by solid filter. The solid is washed by excess water to increase the purity of vanillin product. The wet vanillin go to a dryer to remove remaining water. The final product is dried vanillin with purity more than 99.5 wt%.

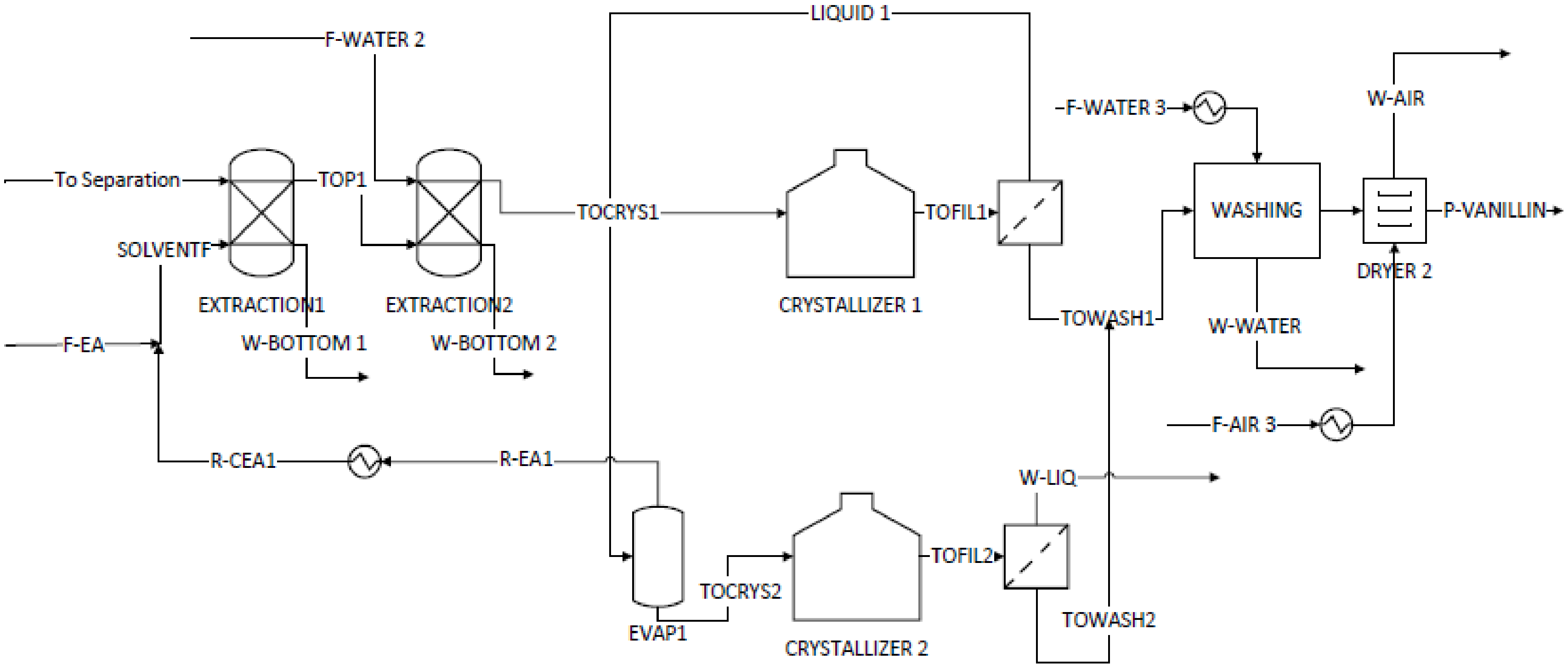


Figure 3.4 Block flow diagram of vanillin separation process pathway 2

3.3.2 Products separation process pathway 2

The second separation pathway is shown in Figure 3-4. Like pathway 1, the pathway 2 starts with extraction column to separate sodium sulfate. The difference is that the pathway 2 has second extraction column using water as solvent to wash and remove remaining sodium sulfate from the products solution.

Table 3-7 Process conditions for two extraction columns in separation process pathway 2

Parameters	Value
Extraction column 1	
Extraction column stages	10
Ethyl acetate (kg/hr)	560
Pressure (bar)	1
Temperature (^{0}C)	80
Extraction column 2	
Extraction column stages	10
Water (kg/hr)	40
Pressure (bar)	1
Temperature (^{0}C)	50

The process conditions of both extraction columns are shown in Table 3-7.

The next step after the extraction is crystallization to separate vanillin from other phenolic compounds. The crystallizer is operated at temperature of 5 °C under atmospheric pressure.

Table 3-8 The solubility of vanillin in Ethyl acetate (extraction solvent) [23]

Temperature, T (^{0}C)	**Solubility (g/l)**
25	216.77
30	225.60
35	234.44
40	243.27
45	252.10
50	260.94
55	269.77
60	278.61
65	287.44
70	296.28

The solubility of vanillin in Ethyl acetate (extraction solvent) used in this study is shown in Table 3-8. After crystallization, vanillin crystal is separated from liquid solution by solid filter. The liquid solution is sent to flash drum unit 2 to recover extraction solvent for recycle. The liquid solution from flash drum unit 2 goes to crystallization unit 2 followed by filter unit 2 to crystallize and separate the remaining vanillin. All the separated vanillin crystal obtained from two filters units are sent to a washing unit to remove remaining impurities from the vanillin product. Finally, the wet vanillin crystal is sent to a dryer to remove remaining water. The final product is dried vanillin with purity is more than 99.5 wt%.

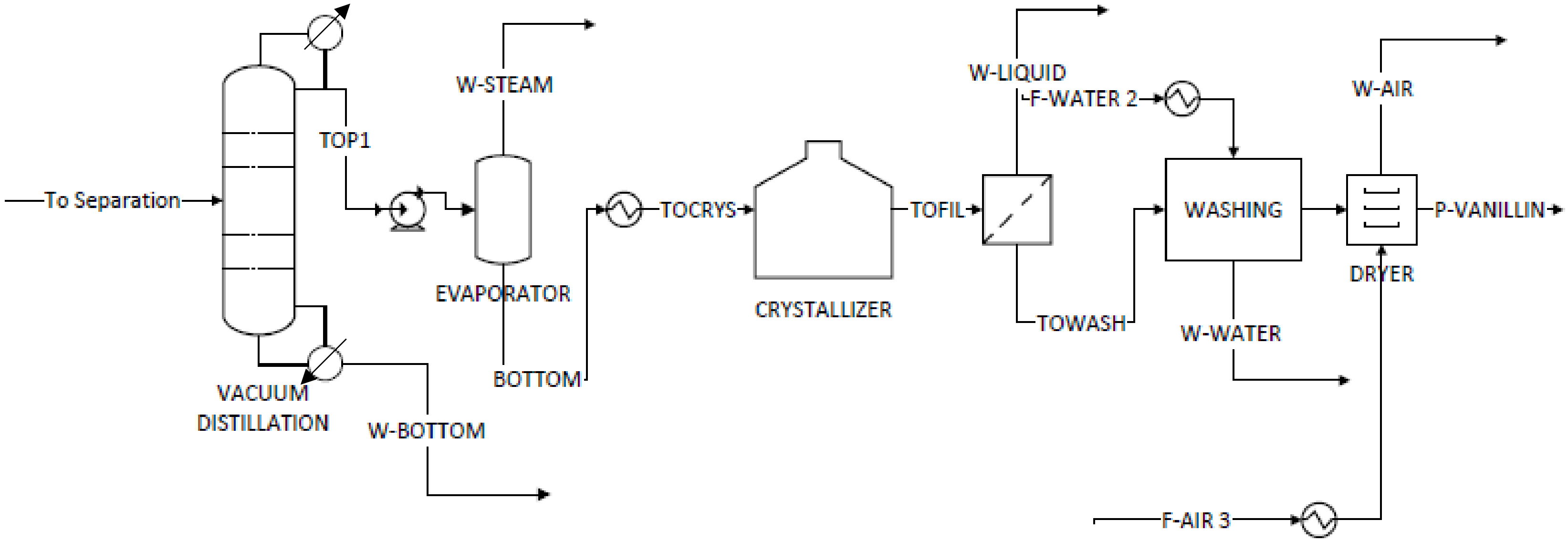


Figure 3-5 Block flow diagram of vanillin separation process pathway 3

3.3.4 Products separation process pathway 3

The last pathway is shown in Figure 3-5. The oxidation products solution after neutralization are sent to vacuum distillation column. The distillation column operate in vacuum condition to separate sodium sulfate from products solution.

Table 3-9 Process conditions of distillation column in separation process pathway 3

Parameters	Value
Distillation column stages	10
Bottoms rate (kg/hr)	2998
Reflux ratio	2
Pressure (kPa)	10

The process condition of this vacuum distillation column is shown in Table 3-9. Distillate from distillation column is passed through a pump to increase pressure from vacuum to atmospheric pressure. After that a crystallizer is used to purify vanillin. The solubility data used in this crystallizer is shown in Table 3-6. The vanillin crystal product is separated by using a solid filter followed by washing unit and dryer as same as other pathways. The final product is dried vanillin crystal with purity more than 99.5 wt%.

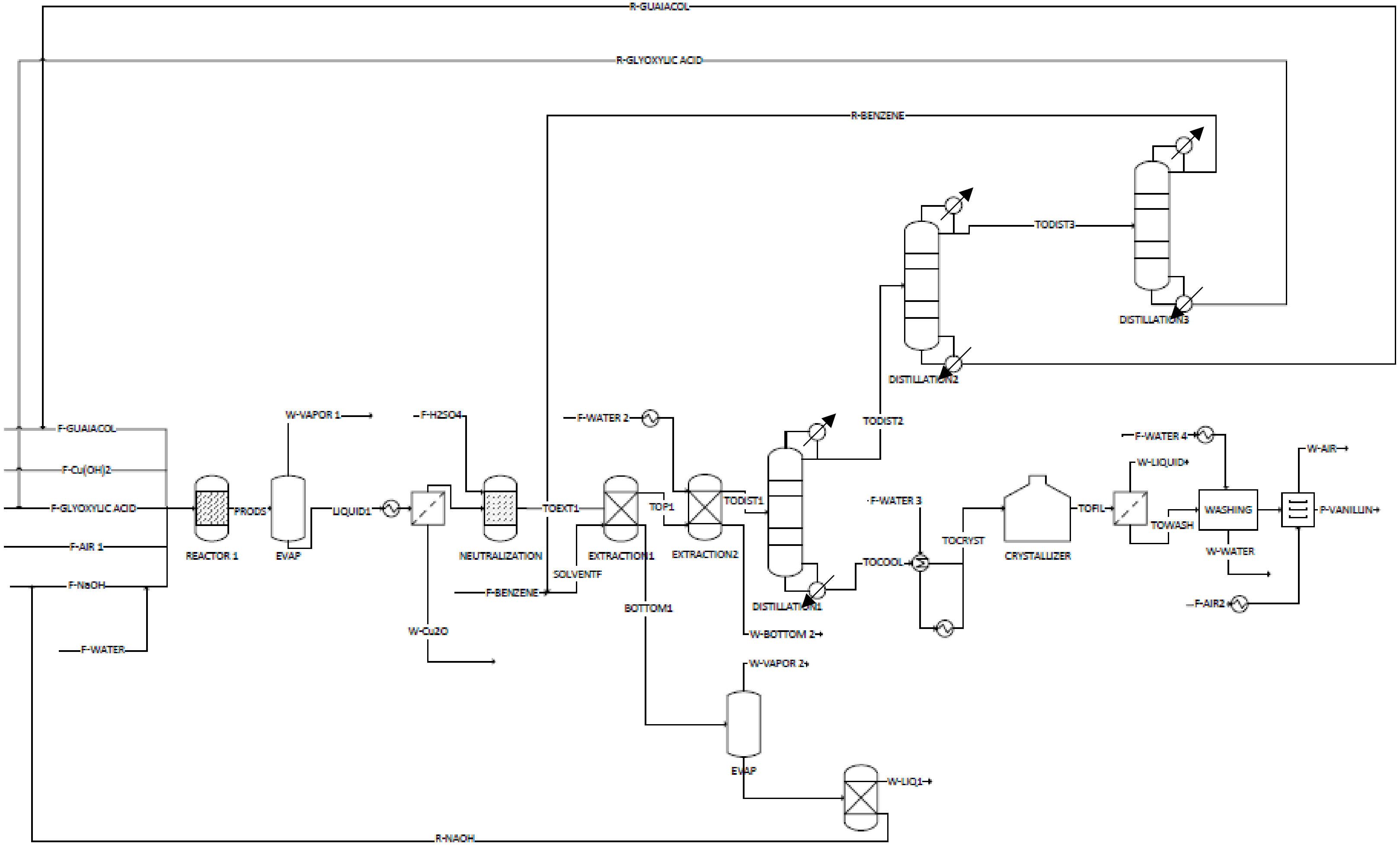


Figure 3-6 Block flow diagram of petrochemical vanillin production process used for simulation

3.3.5 Petrochemical vanillin production process

The commercial vanillin production process typically produces vanillin from guaiacol (petrochemical product) and glyoxylic acid. The reaction step of petrochemical vanillin from guaiacol and glyoxylic acid is shown in Figure 3-7.

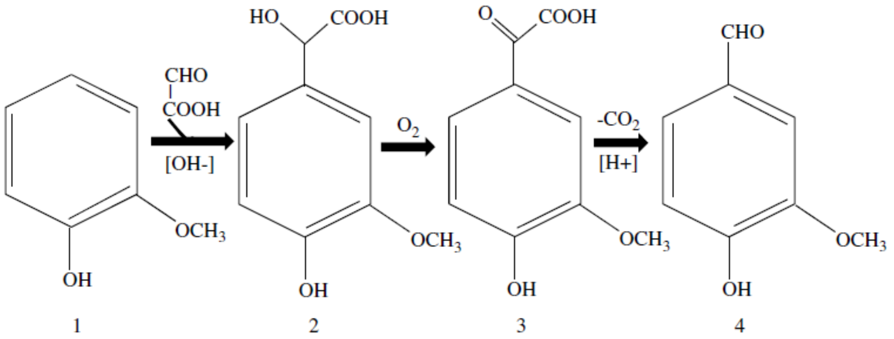


Figure 3-7 The reaction step of petrochemical vanillin from guaiacol and glyoxylic acid. Guaiacol (1) reacts with glyoxylic acid by electrophilic aromatic substitution. The resulting vanillylmandelic acid (2) is then converted via 4-hydroxy-3-methoxyphenylglyoxylic acid (3) to vanillin (4) by oxidative decarboxylation [32]

Table 3-10 Main reactor process conditions

Parameters	Value	Ref.
Reaction 1		
Guaiacol, $C_7H_8O_2$ (kg/hr)	138.60	Set up for final vanillin 100 kg/hr
Glyoxylic acid, $C_2H_2O_3$ (kg/hr)	Equal mole with guaiacol	Kalikar et al. [33]
NaOH (kg/hr)	1,783.84	Kalikar et al. [33]
Reaction conversion	0.75	Kalikar et al. [33]
$\boldsymbol{C_7H_8O_2 + C_2H_2O_3 \rightarrow C_9H_{10}O_5\ (vanillylmandelic\ acid)}$		

Parameters	Value	Ref.
Reaction 2		
Vanillylmandelic acid, $C_9H_{10}O_5$ (kg/hr)	Products from reaction 1	-
Oxidizing reagent, $Cu(OH)_2$ (kg/hr)	143.91	Mass Balance
Air (m^3/hr)	78.64	Kalikar et al. [33]
Reaction conversion	0.88	Kalikar et al. [33]

$$C_9H_{10}O_5 + 2Cu(OH)_2 \xrightarrow{Air} C_8H_8O_3\,(Vanillin) + Cu_2O + 3H_2O + CO_2$$

A block flow diagram of vanillin production from petrochemical pathway is created and simulated in Aspen plus® software as shown in Figure 3-6. It starts with feeding of raw materials to the main reactor. In this reactor, condensation of guaiacol with glyoxylic acid and oxidative decarboxylation of vanillylmandelic acid to produces vanillin takes place. The process conditions of main reactor show in Table 3-10. Products stream from main reactor are fed to flashing process to remove remaining air from products solution. Copper oxide solid (one of products from main reactor) are separated by a solid filter. After that, products solution is neutralized to convert sodium guaiacolate to guaiacol by sulfuric acid. After that, the solution is sent to extraction process.

Table 3-11 Process conditions for extraction column 1 in petrochemical vanillin production process

Parameters	Value
Extraction column stages	10
Benzene (kg/hr)	1500
Pressure (bar)	1
Temperature (^{0}C)	40

Table 3-12 Process conditions for extraction column 2 in petrochemical vanillin production process

Parameters	Value
Extraction column stages	10
Water (kg/hr)	40
Pressure (bar)	1
Temperature (^{0}C)	50

The first extraction column is used to separate remaining raw materials from products solution. The extraction solvent is benzene. In this column, the major portion of sodium hydroxide and sodium sulfate are separated. The process conditions for the first extraction column is shown in Table 3-11. Top stream from the first extraction column is fed to the second extraction column which uses water as a solvent to remove remaining sodium hydroxide from the products stream. The process condition of second extraction column is shown in Table 3-12.

The top products of the second extraction column is fed to the first distillation column to remove unreacted guaiacol (raw material), glyoxylic acid, and benzene from the products solution.

Table 3-13 Process conditions of distillation column 1 in petrochemical vanillin production process

Parameters	Value
Distillation column stages	10
Distillate rate (kg/hr)	1584
Reflux ratio	2
Pressure (bar)	1

The process conditions of first distillation column is shown in Table 3-13. The distillate is fed to the second distillation column to separate benzene and glyoxylic acid from guaiacol. The bottom product obtained from the first distillation column is fed to crystallizer together with water, to produce a saturated solution before crystallizing. The solubility data used in this crystallizer is the same data as presented in Table 3-6. The vanillin crystal separated from solid filter is washed by excess water to remove remaining impurities and the wet vanillin is further dried in a dryer to remove remaining water. At the end, the final product is dried vanillin with purity is more than 99.5 wt%.

Table 3-14 Process conditions of distillation column 2 in petrochemical vanillin production process

Parameters	Value
Distillation column stages	20
Distillate rate (kg/hr)	1550
Reflux ratio	10
Pressure (bar)	1

For the second distillation column, the process condition of this unit is shown in Table 3-14. Distillate stream from this unit containing benzene and glyoxylic acid is sent to the third distillation column for separation. The bottom stream of second distillation column contains guaiacol (raw material) is recycled to the main reactor.

Table 3-15 Process conditions of distillation column 3 in petrochemical vanillin production process

Parameters	Value
Distillation column stages	20
Distilate rate (kg/hr)	1505
Reflux ratio	10
Pressure (bar)	1

The process condition of the third distillation column is shows in Table 3-15.

The distillate stream of third distillation column containing benzene is recycled to first extraction column. The bottom stream from the third distillation column containing glyoxylic acid is recycled to the first reactor as well.

3.4 Techno Economic analysis

The cost estimation of equipment, raw material, and price of products were obtained from literatures. Estimated material costs used in this study are shown in Table 3-16.

Table 3-16 Estimated material costs

No.	Type	Grade	Price ($)/ kg
1	Kraft lignin	Industrial	0.064 [34]
2	NaOH	Industrial	0.3
3	Vanillin (>99.5% purity)	Industrial	20
4	Ethyl Acetate (EA)	Industrial	0.7
5	Sulfuric acid (H_2SO_4)	Industrial	0.15
6	Hydrogen peroxide (H_2O_2)	Industrial	0.3
7	Methanol	Industrial	0.38
8	Guaiacol	Industrial	1.5
9	Glyoxylic acid	Industrial	1
10	Copper (II) hydroxide	Industrial	3.41
11	Tab Water	Industrial	0.00038
12	Benzene	Industrial	0.7

Based on the cost data obtained previously and the optimal reaction process conditions from section 3.2, the Techno-Economic analysis of each separation pathways can be performed. Then, the results from the Techno-Economic analysis, especially the energy consumption and economics data, will be analyzed in order to determine and select the best separation pathway.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter explains and discusses the results of this study. The chapter is separated into four sections. They are setting up based simulation model, finding optimal process conditions, simulation of vanillin production process by Aspen Plus® software, and techno economic analysis.

4.1 Setting up based simulation model

The simulation model used in this study was constructed based on the work of Araújo [11]. They used a model as previously described in chapter 2 to simulate vanillin concentration output from Kraft lignin oxidation and validated their results with the experimental data from the work of Mathias in 1993 [12]. The experiment and simulation process condition are shown in Table 4-1.

Table 4-1 Based experiment process condition from Mathias [12] works

Condition	Value
Experiment number	32
Medium temperature (K)	402.6
Oxygen partial pressure (bar)	3.23
Total pressure (bar)	9.7
Initial NaOH concentration (g/l)	80
Kraft Lignin source	*Pinus spp.* (Westvaco Co.)
Initial Kraft lignin concentration (g/l)	60

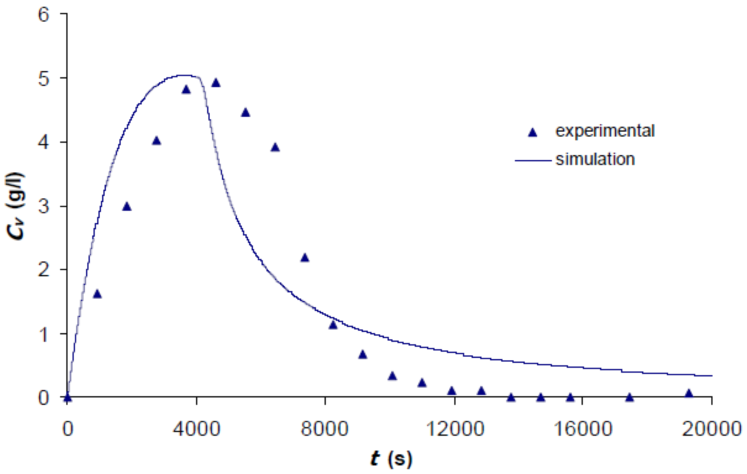


Figure 4-1 Vanillin concentration (C_V) curves for Mathias experiment 32 (Mathias, 1993) and the correspondent simulations considering constant temperature during the reaction and variable phase volumes. [11]

The simulation result and experimental data of Araújo [11] and Mathias [12] is compared and shown in Figure 4-1. From the figure, it can be seen that the developed simulation model as described in chapter 2 is suitable for Kraft lignin oxidation in batch reactor. This is because the simulation result and the experimental data are not much different.

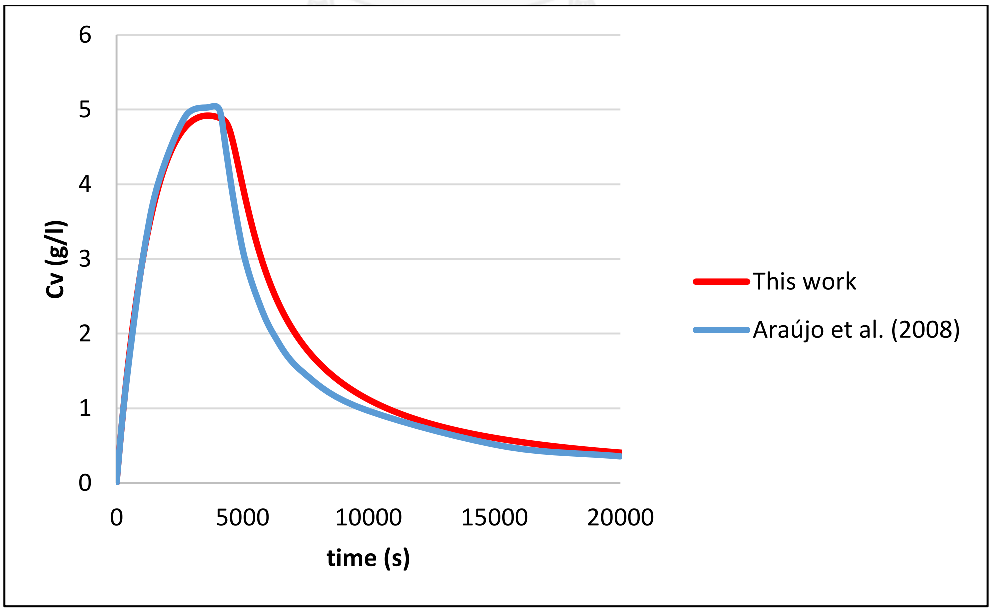


Figure 4-2 The set up based simulation result in this work compare with simulation result of Araújo [12].

The simulation result of this work is shown in Figure 4-2. It can be seen that our result match well with simulation result of Araújo [11]. So, our constructed model is accurate and can be used to study further.

4.2 Finding optimal process conditions

The operating process parameters of Kraft lignin oxidation in batch reactor to be optimized in this study are oxygen partial pressure, initial concentration of feed lignin and reaction temperature. This reaction model used in this study was isothermal and the following assumptions were made [11]:

- Temperature in reactor is constant over the entire reaction time
- The reactor is a perfectly mixed reactor
- Constant volume of liquid and gas
- Closed system
- Constant total pressure
- Oxidation reaction is irreversible
- Mass transfer in reaction is negligible

4.2.1 Oxygen partial pressure

The effect of oxygen partial pressure was studied by keeping the reaction temperature at 130 °C to follow the study of Mathias [12]. Oxygen partial pressure and reaction temperature were varied to find the optimal condition. The setting of process conditions are shown in Table 4-2.

Table 4-2 The setting process conditions for the optimal oxygen partial pressure finding

Process condition	Value
Initial feed lignin concentration (g/l)	60
Reaction temperature (^{0}C)	130
Oxygen partial pressure (bar)	1-5

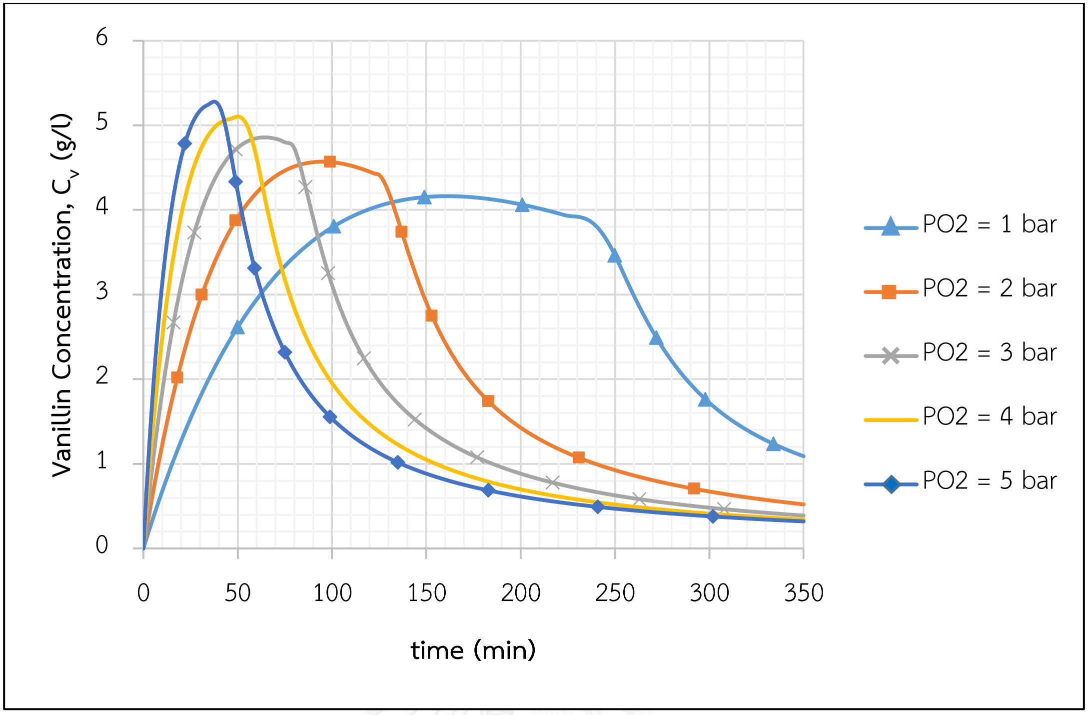


Figure 4-3 the effect of feed oxygen partial pressure (P_{O2}) to vanillin concentration (C_v)

Figure 4-3 shows the effect of feed oxygen partial pressure (P_{O2}) to vanillin concentration (C_v) by keeping the reaction temperature at 130 °C and initial Kraft lignin concentration at 60 g/l. X-axis is reaction time and y-axis is concentration of vanillin.

From Figure 4-3, it is shown that increasing oxygen partial pressure leads to increased vanillin concentration and decreased reaction time, and so higher vanillin yield can be achieved. This result can be explained by the rate of reaction of lignin oxidation as presented in equation (3). It can be noticed that when the oxygen partial pressure is higher than 3 bar, the amount of vanillin increases less than 0.5%. This is because when the oxygen concentration is too high, some portion of the vanillin product will start to degrade. As a result, the vanillin yield increase at a lower rate.

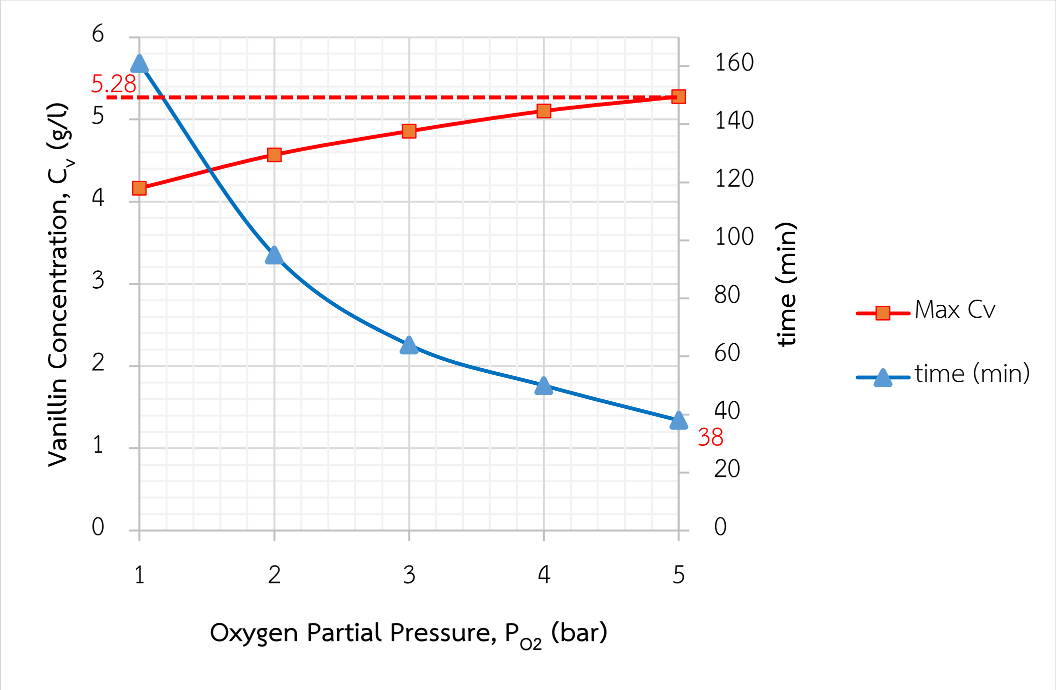


Figure 4-4 The effect of oxygen partial pressure to maximum vanillin concentration (Cv) and reaction time

Figure 4-4 shows the maximum vanillin concentration and reaction time in y-axis and oxygen partial pressure in x-axis. This graph is used to find the optimal oxygen partial pressure for vanillin production. From Figure 4-4, the selected optimal oxygen partial pressure is 5 bars, at reaction temperature of 130 ^{0}C. From this condition, the maximum vanillin yield is 8.80% and the reaction time is only 38 minutes. Compared with the experimental data by Mathias [12] in Figure 4-1 in which they used oxygen partial pressure at 3.23 bars and the reaction temperature at 129 ^{0}C. They obtained the maximum vanillin yield at 8.28% for 77 minutes of operation. It can be seen that our selected condition of 5 bars of oxygen partial pressure could only offer a slightly higher vanillin yield. However, our reaction time is halved and that would mean our production capacity is about double.

4.2.2 Initial concentration of feed lignin

The optimal initial concentration of feed lignin (C_{Li}) is studied by keeping the reaction temperature at 130 $^{\circ}$C and oxygen partial pressure at 5 bars. Initial lignin concentration was varied to find the optimal value. The setting process conditions for the optimal initial lignin concentration finding are shown in Table 4-3.

Table 4-3 The setting process conditions for the optimal initial lignin concentration finding

Process condition	Value
Initial feed lignin concentration (g/l)	30-120
Reaction temperature (^{0}C)	130
Oxygen partial pressure (bar)	5

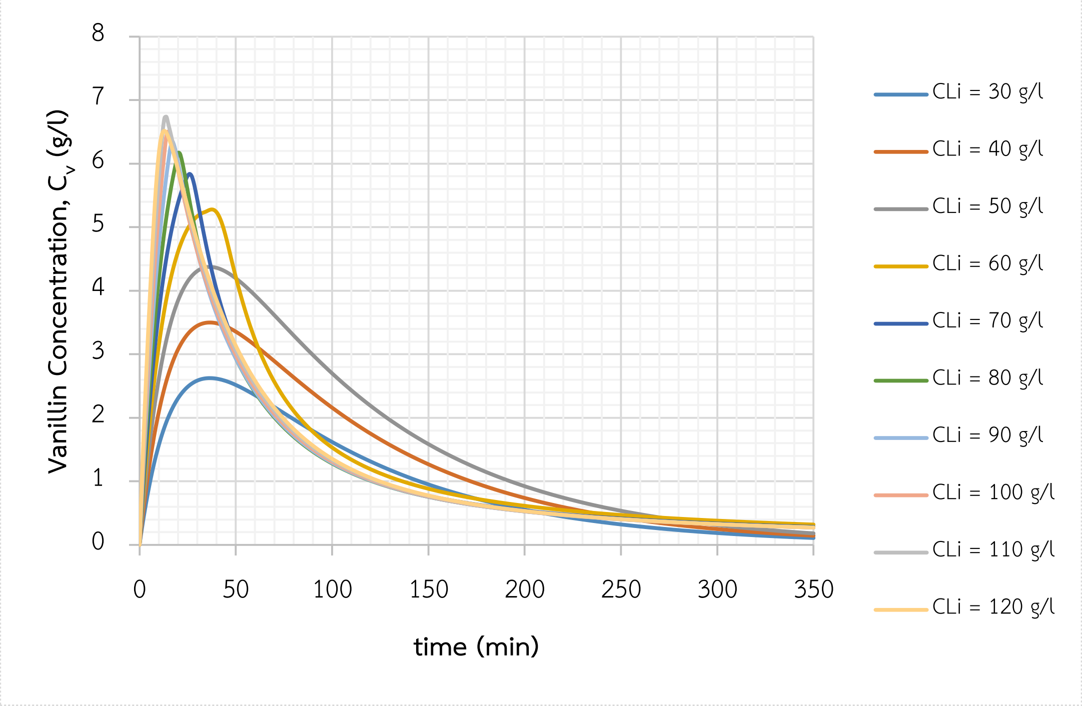


Figure 4-5 The effect of Initial concentration of feed lignin to vanillin concentration

Figure 4-5 shows the effect of Initial concentration of feed lignin to vanillin concentration by keeping the reaction temperature at 130 °C and oxygen partial pressure at 5 bars. X-axis is reaction time and y-axis is Initial concentration of feed lignin.

From Figure 4-5, it is shown that increasing initial concentration of feed lignin increases vanillin concentration decreases reaction time. This effect corresponds to the reaction rate of Kraft lignin oxidation (equation 3 and 19 as presented in chapter 2) which showed that vanillin concentration is directly varied with initial feed lignin concentration. However, the vanillin concentration can be decreased if lignin concentration in feed is too much. This is because the excess lignin reduces the reaction area so, the vanillin occurs harder.

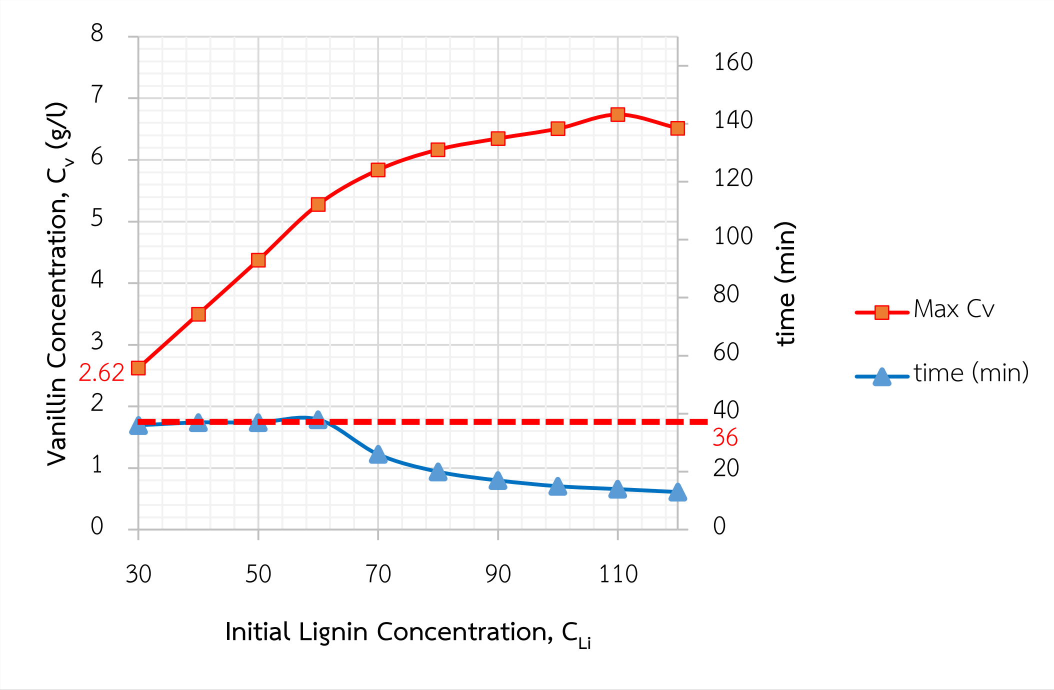


Figure 4-6 The effect of initial feed lignin concentration (C_{Li}) to maximum vanillin concentration (C_V) and reaction time

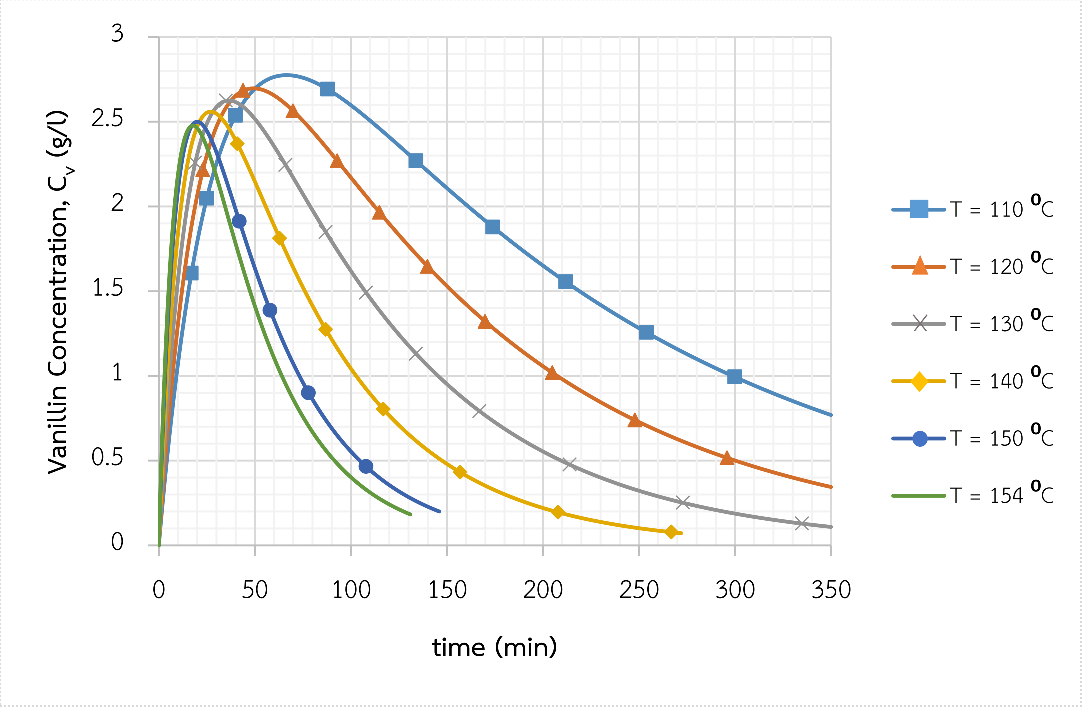
Figure 4-6 shows the effect of initial feed lignin concentration (x-axis) to the maximum vanillin concentration and reaction time in y-axis. According to limitation of vanillin production model described in chapter 2, the variation range of initial feed lignin concentration can be varied in the range of 30-120 g/l only. From this range, the most suitable initial feed lignin concentration is 30 g/l at reaction temperature of 130 ^{0}C and oxygen partial pressure of 5 bar. This condition gives vanillin concentration of 8.75% for 36 minutes of operating time. Although the vanillin yield obtained from 30 g/l of initial lignin concentration is slightly less than the yield obtained from 60 g/l of feed lignin and it takes slightly longer time. But using 30 g/l of feed lignin concentration can save a lot of more raw material and will eventually and significantly increase economic viability of the process. So, the optimal initial concentration of feed lignin at 30 g/l is selected.

4.2.3 Reaction temperature

The optimal reaction temperature is studied by keeping initial lignin concentration at 30 g/l and oxygen partial pressure at 5 bars. The reaction temperature was varies to find optimal value. The setting process conditions for the optimal reaction temperature finding are shown in Table 4-4.

Table 4-4 The setting process conditions for the optimal reaction temperature finding

Process condition	Value
Initial feed lignin concentration (g/l)	30
Reaction temperature (^{0}C)	110-154 (6)
Oxygen partial pressure (bar)	5



.**Figure 4-7** The effect of reaction temperature to vanillin concentration

Figure 4-7 shows the effect of reaction temperature to vanillin concentration by set initial concentration of feed lignin is 30 g/l and oxygen partial pressure is 5 bars. X-axis is reaction time and y-axis is reaction temperature.

From Figure 4-7, it shows that increasing reaction temperature decreases vanillin concentration and reaction time. This is because at higher temperature the vanillin compound formed from the oxidation reaction will degrade at a higher rate. As a result, the total vanillin yield is decreased. It can be noticed that vanillin concentration is not much decreased when increasing reaction temperature every 10 °C. The decreasing vanillin yield is not more than 0.5%. This is because the reaction temperature can affect the vanillin product concentration but that effect is less influenced when comparing with the effect of oxygen partial pressure and feed lignin concentration.

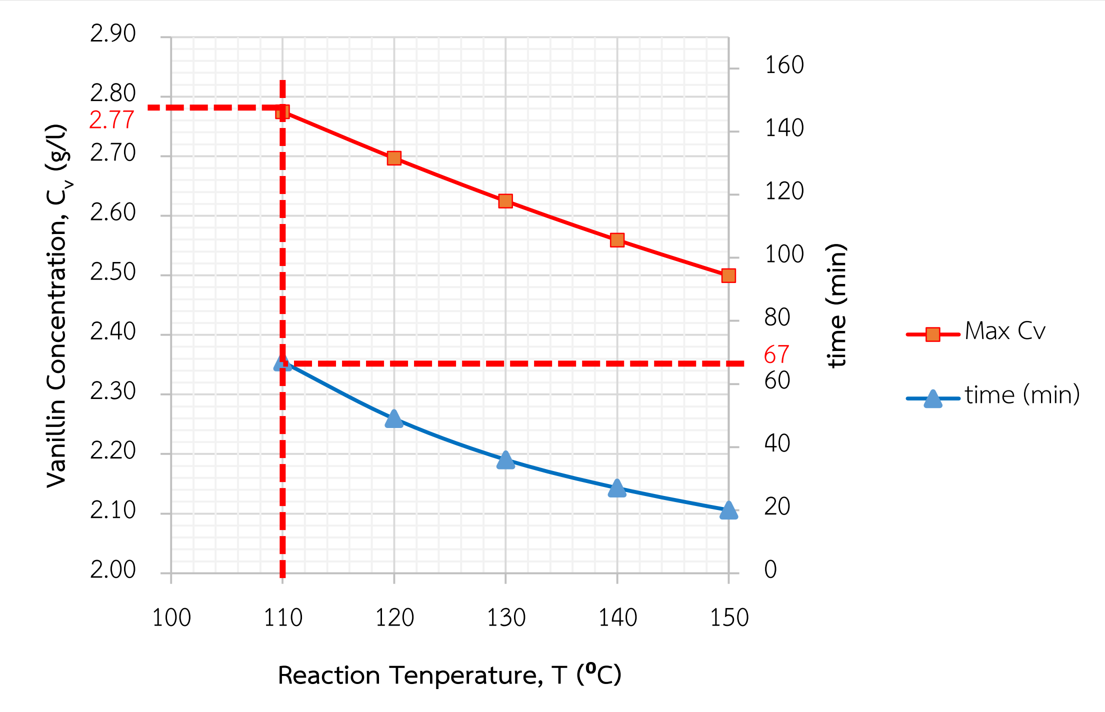


Figure 4-8 The effect of reaction temperature to maximum vanillin concentration and reaction time

Figure 4-8 shows the effect of reaction temperature (x-axis) to the maximum vanillin concentration (C_v) and reaction time in y-axis. The selected optimal reaction temperature is 110 ℃ at 5 bar of oxygen partial pressure and 30 g/l of feed lignin concentration. This process condition gives 9.25% maximum vanillin yield at 67 minutes of reaction time.

Table 4-5 The optimal process condition for Kraft lignin oxidation in batch reactor

Process condition	**Value**
Oxygen partial pressure (bar)	5
Initial concentration of feed lignin (g/l)	30
Reaction temperature (^{0}C)	110

The conclusion of selected optimal process conditions in this study is shown in Table 4-5.

Table 4-6 The comparison between process conditions and result from Mathias [12] experiment and this work

Condition	**Mathias [12] experiment 32**	**This work**
Oxygen partial pressure (bar)	3.23	5
Initial concentration of feed lignin (g/l)	60	30
Reaction temperature (^{0}C)	130	110
Maximum vanillin yield (%)	8.71	9.25
Reaction time (min)	64	67

The comparison between process conditions and result from Matias [12] experiment and this work is shown in Table 4-6. It can be seen that the selected optimal process conditions of this work give higher vanillin yield at slightly higher operating time. It can also save a lot of feed lignin raw material and energy requirement because the feed lignin concentration and reaction temperature are lower.

4.3 Simulation of vanillin production process by Aspen Plus® software

Vanillin production from Kraft lignin oxidation process in this study is simulated by Aspen Plus® software. The oxygen partial pressure, initial lignin concentration, and reaction used in this simulation were obtained from the optimal process conditions from section 4.2. The simulation contains main reaction process and separation process in three pathways. The three separation process pathways are as follows.

- 1 stage solvent extraction, distillation and crystallization
- 2 stages solvent extraction and crystallization
- Vacuum distillation and crystallization

The performance of each separation pathway is considered from energy consumption and economic analysis. The results of vanillin production from Kraft lignin pathways are compared with the result of vanillin production from petrochemical pathway as well.

4.3.1 Simulation results of vanillin production from Kraft lignin with separation pathway 1

From Figure 3-2, the main oxidation reactor produces vanillin for the amount of 111.32 kg/hr (to get vanillin final product 100 kg/hr and equivalent to 9.25 %yield of feed lignin) from the selected optimal process conditions found in section 4-2 (P_{O2} = 5 bar and T = 110 °C). The reactor output includes vanillin product, unreacted lignin, oxidized lignin, water, oxygen, nitrogen, sodium hydroxide and other phenolic compounds like vanillic acid, syringaldehyde, acetovanillone and p-hydroxybenzaldehyde.

Table 4-7 Mass balance simulation result around main oxidation reactor of the separation pathway 1

No.	**Components**	**Input**	**Output**	**Output Yield (mass)**
		Value (kg/hr)	Value (kg/hr)	
1	Water	37,936.41	37,936.41	0.92650
2	Oxygen gas	42.21	2.00	0.00005
3	Nitrogen gas	158.78	160.27	0.00391
4	Vanillin	-	111.32	0.00272
5	Vanillic acid	-	31.24	0.00076
6	Syringaldehyde	-	8.43	0.00021
7	Acetovanillone	-	77.03	0.00188
8	p-Hydroxybenzaldehyde	-	6.02	0.00015
9	Kraft Lignin	1,203.64	129.86	0.00317
10	NaOH	1,604.85	1,604.85	0.03919
11	SO_2	-	6.69	0.00016
12	Oxidized Lignin	-	842.04	0.02056
13	H_2O Occur	-	29.73	0.00073

Mass balance simulation result around the main oxidation reactor is shown in Table 4-7. The output yields are obtained by using RYIELD reactor model in Aspen Plus® software.

Table 4-8 The mass balances simulation results of the separation pathway 1

Mass Flow kg/hr	To Separation	F-EA	SOLVENTF	TOP1	W-BOTTOM	R-EA	BOTTOM2
WATER	10872.135	-	11.471	24.067	10859.539	11.471	12.592
OXYGEN	0.001	-	-	-	0.001	-	-
VANILLIN (l)	110.328	-	-	110.328	-	-	110.328
NITROGEN	0.039	-	0.001	0.001	0.039	0.001	-
VANILLIC ACID	30.443	-	-	30.443	-	-	30.443
SYRINGALDEHYDE	4.655	-	-	4.655	-	-	4.655
SO_2	0.088	-	0.002	0.002	0.088	0.002	-
ACETOVANILLONE	76.390	-	-	76.390	-	-	76.390
p-Hydroxybenzaldehyde	5.971	-	-	5.971	-	-	5.971
NaOH	0.007	-	-	-	0.007	-	-
VANILLIN (s)	-	-	-	-	-	-	-
ETHYL ACETATE	-	452.474	531.000	78.882	452.118	78.526	0.360
Na_2SO_4	2827.744	-	-	6.260	2821.484	-	6.260
Temperature (C)	**80**	**25**	**32**	**71.4**	**70**	**84.4**	**134.7**
Mass Flow kg/hr	**13927.801**	452.474	**542.474**	**336.999**	**14133.3**	**90**	**246.999**
Enthalpy MJ/hr	**-1.97E+05**	**-2.47E+03**	**-3.07E+03**	**-1.50E+03**	**-1.99E+05**	**-5.98E+02**	**-8.56E+02**

Table 4-8 The mass balances simulation results of the separation pathway 1 (Con't)

Mass Flow kg/hr	F-WATER2	TOCRYS	TOFIL	W-LIQUID	TOWASH	WETVANIL	P-VANILLIN
WATER	3154.949	12.592	3167.541	3156.939	10.602	0.584	0.538
OXYGEN	-	-	-	-	-	-	-
VANILLIN (l)	-	110.328	10.845	10.809	0.036	0.001	0.001
NITROGEN	-	-	-	-	-	-	-
VANILLIC ACID	-	30.443	30.443	30.341	0.102	0.003	0.003
SYRINGALDEHYDE	-	4.655	4.655	4.640	0.016	-	-
SO_2	-	-	-	-	-	-	-
ACETOVANILLONE	-	76.390	76.390	76.134	0.256	0.007	0.007
p-Hydroxybenzaldehyde	-	5.971	5.971	5.951	0.020	0.001	0.001
NaOH	-	-	-	-	-	-	
VANILLIN (s)	-	-	99.482	-	99.482	99.482	99.482
ETHYL ACETATE	-	0.360	0.360	0.359	0.001	-	-
Na_2SO_4	-	6.260	6.260	6.239	0.021	0.001	0.001
Temperature (C)	**25**	**55**	**5**	**5**	**5**	**5**	**12**
Mass Flow kg/hr	**3154.949**	**246.999**	**3401.948**	**3291.412**	**110.536**	**100.079**	**100.033**
Enthalpy MJ/hr	**-5.01E+04**	**-8.95E+02**	**-5.10E+04**	**-5.08E+04**	**-1.73E+02**	**-1.16E+01**	**-1.06E+01**

The mass balance simulation results of first separation pathway is shown in Table 4-8. From Figure 3-3 and Table 4-8, the products stream from main reactor go to separation process. The first step is a flash drum to remove gaseous components such as oxygen, nitrogen and sulfur dioxide (very small amount). After that, the products stream is neutralized by sulfuric acid to adjust pH of the solution from base to neutral. For this study, it is assumed that all unreacted lignin and oxidized lignin coagulate and are removed by a solid filter. After solid filtration, the product stream contains vanillin, sodium sulfate, water and other phenolic compounds. The separation process pathways 1 contains liquid extraction, distillation and crystallization process.

After passing the flash drum unit, the product stream goes at top of extraction column and ethyl acetate (extraction solvent) is fed at the bottom of the column. From Table 4-8, it can be seen that most amount of sodium sulfate, water and ethyl acetate go to the W - BOTTOM stream while the TOP1 stream contains vanillin, other phenolic compounds and some ethyl acetate. This is because sodium sulfate is very soluble in water and most amount of water goes to W-BOTTOM stream while the vanillin and other phenolic compounds can dissolve in ethyl acetate better than water. Just a small amount of ethyl acetate can separate vanillin and phenolic compounds from the water. Sodium sulfate can dissolve in water better than vanillin and phenolic compounds so, it is separated and goes to the bottom outlet of extraction column.

The TOP1 stream goes to the distillation column for separation of ethyl acetate from vanillin and other phenolic compounds. Most amount of ethyl acetate is separated to the top of the distillation column because the boiling point of ethyl acetate is much lower than those of vanillin and other phenolic compounds. Ethyl acetate that exits at the top stream of distillation column (R-EA) is fed to a solvent tank for recycle. Vanillin and other phenolic compounds stream from the bottom of distillation column go to a crystallizer. For the crystallization, the crystallizing solvent used in this pathway is water. From the vanillin in total feed to crystallizer at 110.33 kg/hr, the vanillin crystal at 99.48 kg/hr can be obtained. The percentage of crystallization is 90.17%. The amount of vanillin product after drying process is 100.033 kg/hour with 99.5% purity.

4.3.2 Simulation results of vanillin production from Kraft lignin with separation pathway 2

From Figure 3-2, the main oxidation reactor produces vanillin for the amount of 112.68 kg/hr (to get vanillin final 100 kg/hr and equivalent to 9.25 %yield of feed lignin) from the selected optimal process conditions found in section 4-2 (P_{O2} = 5 bar and T = 110 $^{\circ}$C).

Table 4-9 Mass balance simulation result around main oxidation reactor of the separation pathway 2

No.	**Components**	**Input**	**Output**	**Output Yield**
		Value (kg/hr)	Value (kg/hr)	**(mass)**
1	H_2O	38,400.83	38,400.83	0.92650
2	O_2	42.69	2.00	0.00005
3	N_2	160.61	162.11	0.00391
4	Vanillin	-	112.68	0.00272
5	Vanillic acid	-	31.63	0.00076
6	Syringaldehyde	-	8.53	0.00021
7	Acetovanillone	-	77.98	0.00188
8	p-Hydroxybenzaldehyde	-	6.09	0.00015
9	Lignin	1,218.37	131.45	0.00317
10	NaOH	1,624.50	1624.50	0.03919
11	SO_2	-	6.77	0.00016
12	Oxidized Lignin	-	852.35	0.02056
13	H_2O Occur	-	30.09	0.00073

Mass balance simulation result around the main oxidation reactor in this pathway is shown in Table 4-9. The output yields are obtained by using RYIELD reactor model in Aspen Plus® software.

Table 4-10 The mass balances simulation results of the separation pathway 2

Mass Flow kg/hr	**To Separation**	**F-EA**	**SOLVENTF**	**TOP1**	**W-BOTTOM1**	**F-WATER2**	**TOCRYS1**
WATER	11005.704	-	6.472	24.316	10987.860	40.000	25.479
OXYGEN	-	-	-	-	0.001	-	-
VANILLIN (l)	111.679	-	0.001	111.679	-	-	111.201
NITROGEN	0.039	-	-	0.001	0.039	-	-
VANILLIC ACID	30.815	-	-	30.815	-	-	30.815
SYRINGALDEHYDE	4.712	-	-	4.712	-	-	4.712
SO_2	0.090	-	0.001	0.002	0.089	-	0.002
ACETOVANILLONE	77.325	-	0.001	77.327	-	-	77.252
p-Hydroxybenzaldehyde	6.044	-	-	6.044	-	-	6.022
NaOH	0.005	-	-	-	0.005	-	-
VANILLIN (s)	-	-	-	-	-	-	-
ETHYL ACETATE	-	516.470	560.000	102.982	457.018	-	102.756
Na_2SO_4	2862.364	-	-	6.324	2856.040	-	0.025
Temperature (C)	**80**	**25**	**28.5**	**71.3**	**69.9**	**25**	**61.7**
Mass Flow kg/hr	**14098.779**	**516.47**	**566.476**	**364.203**	**14301.05**	**40**	**358.264**
Enthalpy MJ/hr	**-2.00E+05**	**-2.82E+03**	**-3.15E+03**	**-1.64E+03**	**-2.01E+05**	**-6.35E+02**	**-1.61E+03**

Table 4-10 The mass balances simulation results of the separation pathway 2 (Con’t)

Mass Flow kg/hr	**W-BOTTOM2**	**TOFIL1**	**LIQUID1**	**TOWASH1**	**R-CEA1**	**TOCRYS2**
WATER	38.837	25.479	24.516	0.963	6.472	18.043
OXYGEN	-	-	-	-	-	-
VANILLIN (l)	0.479	20.277	19.511	0.766	0.001	19.510
NITROGEN	-	-	-	-	-	-
VANILLIC ACID	-	30.815	29.651	1.164	-	29.651
SYRINGALDEHYDE	-	4.712	4.534	0.178	-	4.534
SO_2	-	0.002	0.002	-	0.001	-
ACETOVANILLONE	0.075	77.252	74.333	2.919	0.001	74.331
p-Hydroxybenzaldehyde	0.022	6.022	5.795	0.228	-	5.795
NaOH	-	-	-	-	-	-
VANILLIN (s)	-	90.923	-	90.923	-	-
ETHYL ACETATE	0.226	102.756	98.873	3.883	43.530	55.337
Na_2SO_4	6.300	0.025	0.024	0.001	-	0.024
Temperature (C)	**71.3**	**5**	**5**	**5**	**70**	**85.2**
Mass Flow kg/hr	**45.939**	**358.264**	**257.238**	**101.026**	**50.006**	**207.225**
Enthalpy MJ/hr	**-6.69E+02**	**-1.36E+03**	**-1.30E+03**	**-5.38E+01**	**-3.33E+02**	**-9.25E+02**

Table 4-10 The mass balances simulation results of the separation pathway 2 (Con’t)

Mass Flow kg/hr	**TOFIL2**	**W-LIQ**	**TOWASH2**	**WETVANIL**	**P-VANILLIN**
WATER	18.043	17.957	0.087	0.313	0.303
OXYGEN	-	-	-	-	-
VANILLIN (l)	10.920	10.867	0.052	0.023	0.023
NITROGEN	-	-	-	-	-
VANILLIC ACID	29.651	29.508	0.142	0.037	0.037
SYRINGALDEHYDE	4.534	4.512	0.022	0.006	0.006
SO_2	-	-	-	-	-
ACETOVANILLONE	74.331	73.974	0.357	0.093	0.093
p-Hydroxybenzaldehyde	5.795	5.767	0.028	0.007	0.007
NaOH	-	-	-	-	-
VANILLIN (s)	8.591	-	8.591	99.514	99.514
ETHYL ACETATE	55.337	55.071	0.266	0.118	0.049
Na_2SO_4	0.024	0.023	-	-	-
Temperature (C)	**5**	**5**	**5**	**5.4**	**14.8**
Mass Flow kg/hr	**207.225**	**197.68**	**9.545**	**100.111**	**100.032**
Enthalpy MJ/hr	**-9.37E+02**	**-9.32E+02**	**-4.22E+00**	**-8.45E+00**	**-6.34E+00**

In this pathway, the simulation of reaction of Kraft lignin oxidation is the same as the separation pathway 1. The differences of the two pathways are found in separation section.

The mass balance simulation results of second separation pathway is shown in Table 4-10. From Figure 3-4 and Table 4-10, products stream is sent to the first extraction column to separate sodium sulfate from a product stream, same as the separation pathway 1. But in the pathway 2, a second extraction column is used for washing all remaining sodium sulfate from the product stream. The remaining salt in products stream after the first extraction column is 6.32 kg/hr. This amount of salt is removed by excess water in the second extraction column. The solubility of sodium sulfate in water in much better than ethyl acetate and phenolic compound solution. So, all remaining salt can be removed from main products stream by excess water. After that, the products stream containing vanillin and other phenolic compounds go to the first crystallization. The other difference between first and second separation pathway is crystallizing solvent used in the second pathway is remaining ethyl acetate (extraction solvent) in the product stream instead of feed water like first separation pathway. After the first crystallization unit, vanillin crystal at 90.92 kg/hr is obtained from total vanillin in products solution feed of 111.20 kg/hr. The percentage of crystallization is 81.76% which is less than the percentage of crystallization unit in first separation pathway. This is because the solubility of vanillin in ethyl acetate at 5 °C (crystallization temperature) is 181.43 g/l (Table 3-8) that it is much higher than the solubility of vanillin in water (3.69 g/l from Table 3-6). So, vanillin can coagulate to be crystal in water more than vanillin crystal in ethyl acetate at same crystallization temperature. After the first crystallization unit, there is still some considerable amount of vanillin left in the solvent. Therefore, the second crystallization unit is required to produce more vanillin crystal. A flash drum unit before the second crystallization unit is also required to remove some ethyl acetate, to make more vanillin crystal in the second crystallization unit. The amount of vanillin product after drying 100.032 kg/hr with 99.5% purity is obtained. The vanillin separation efficiency of the second separation pathway is lower than that of the first separation pathway. This is because some vanillin is lost in the second extraction column and some vanillin coagulates in ethyl acetate less than water as well. So, to get the same amount of final vanillin product, more feed is needed in the second separation pathway.

4.3.3 Simulation results of vanillin production from Kraft lignin with separation pathway 3

From Figure 3-2, the main oxidation reactor produces vanillin for the amount of 115.05 kg/hr (to get vanillin final product 100 kg/hr and equivalent to 9.25 %yield of feed lignin) from the selected optimal process conditions found in section 4-2 (P_{O2} = 5 bar and T = 110 °C).

Table 4-11 Mass balance simulation result around main oxidation reactor of the separation pathway 3

No.	Components	Input	Output	Output Yield
		Value (kg/hr)	Value (kg/hr)	(mass)
1	Water	39,209.26	39,209.26	0.92651
2	Oxygen gas	43.55	2.00	0.00005
3	Nitrogen gas	163.83	165.37	0.00391
4	Vanillin	-	115.05	0.00272
5	Vanillic acid	-	32.29	0.00076
6	Syringaldehyde	-	8.71	0.00021
7	Acetovanillone	-	79.62	0.00188
8	p-Hydroxybenzaldehyde	-	6.22	0.00015
9	Lignin	1,244.02	134.21	0.00317
10	NaOH	1,658.70	1,658.70	0.03919
11	SO_2	-	6.91	0.00016
12	Oxidized Lignin		870.29	0.02056
13	H_2O Occur	-	30.71	0.00073

Table 4-12 The mass balances simulation results of the separation pathway 3

Mass Flow kg/hr	To Separation	TOP1	W-BOTTOM	W-STEAM	TOCRYS
WATER	11227.204	11227.204	-	8088.548	3138.656
OXYGEN	0.001	0.001	-	0.001	-
VANILLIN (l)	114.028	110.279	3.749	0.123	110.156
NITROGEN	0.040	0.040	-	0.040	-
VANILLIC ACID	31.463	0.000	31.463	0.000	-
SYRINGALDEHYDE	4.811	0.032	4.779	0.032	-
SO_2	0.091	0.091	-	0.090	0.001
ACETOVANILLONE	78.952	32.273	46.679	0.019	32.253
p-Hydroxybenzaldehyde	6.172	0.001	6.171	-	0.001
NaOH	22.473	-	22.473	-	-
VANILLIN (s)	-	-	-	-	-
Na_2SO_4	2882.686	-	2882.685	-	-
Temperature (C)	**80**	**45.3**	**378.3**	**99.8**	**55**
Mass Flow kg/hr	**14367.921**	**11369.921**	**2997.999**	**8088.853**	**3281.067**
Enthalpy MJ/hr	**-2.03E+05**	**-1.78E+05**	**-2.64E+04**	**-1.08E+05**	**-4.99E+04**

Table 4-12 The mass balances simulation results of the separation pathway 3 (Con't)

Mass Flow kg/hr	**TOFIL**	**W-LIQUID**	**TOWASH**	**WETVANIL**	**P-VANILLIN**
WATER	3138.656	3127.746	10.910	0.593	0.495
OXYGEN	-	-	-	-	-
VANILLIN (l)	10.622	10.585	0.037	0.001	0.001
NITROGEN	-	-	-	-	-
VANILLIC ACID	-	-	-	-	-
SYRINGALDEHYDE	-	-	-	-	-
SO_2	0.001	0.001	-	-	-
ACETOVANILLONE	32.253	32.141	0.112	0.003	0.003
p-Hydroxybenzaldehyde	0.001	0.001	-	-	-
NaOH	-	-	-	-	-
VANILLIN (s)	99.534	-	99.534	99.534	99.534
Na_2SO_4	-	-	-	-	-
Temperature (C)	**5**	**5**	**5**	**5.1**	**47.7**
Mass Flow kg/hr	**3281.067**	**3170.474**	**110.594**	**100.131**	**100.033**
Enthalpy MJ/hr	**-5.02E+04**	**-5.00E+04**	**-1.77E+02**	**-1.16E+01**	**-5.28E+00**

Mass balance simulation result around the main oxidation reactor in this pathway is shown in Table 4-11. The output yields are obtained by using RYIELD reactor model in Aspen Plus$^{®}$ software.

The main reaction simulation of Kraft lignin oxidation is the same as the separation pathway 1 and 2. The difference in simulation lies in separation section. From Figure 3-5 and Table 4-12, the products stream goes to vacuum distillation unit to remove sodium sulfate. The boiling point of sodium sulfate is much higher than those of vanillin and other phenolic compounds. So, the sodium sulfate is separated and exit at the bottom of the distillation column. For vacuum distillation, vanillin and other phenolic compounds are distilled under reduced pressure. So, this solution can be distilled at a lower temperature than the required temperature from atmospheric pressure, and consequently with less chance of decomposition. After the vacuum distillation, water, vanillin and other phenolic compound solution go to pump to increase pressure to atmospheric pressure for crystallization in the next step. The crystallizing solvent of this separation pathway is water as same as the separation pathway 1. Before crystallization, some amount of remaining water in products stream is removed by evaporation unit. The amount of vanillin produced after drying is 100.033 kg/hr with 99.5% purity. It should be noted that the vanillin separation efficiency of the third separation pathway is lower than that of the first separation pathway. This is because of the loss of some vanillin in the vacuum distillation column.

4.3.4 Simulation results of vanillin production from petrochemical pathway

This section shows the mass balances of all components around each unit of the vanillin production from petrochemical pathway. This pathway was designed to produce vanillin product at 100 kg/hr, same production capacity as the Kraft lignin pathway.

Table 4-13 The mass balances simulation results of vanillin production from petrochemical pathway

Mass Flow kg/hr	F-GUAIACOL	F-GLYOXYLIC ACID	F-NAOH	F-WATER	R-NAOH	F-CU(OH)2	F-AIR 1
WATER	-	82.658	-	1498.441	-	-	-
O_2	-	-	-	-	-	-	19.163
N_2	-	-	-	-	-	-	72.090
VANILLIN (l)	-	-	-	-	-	-	-
GUAIACOL	105.593	-	-	-	-	-	-
NaOH	-	-	22.542	-	1768.551	-	-
VANILLIN (s)	-	-	-	-	-	-	-
BENZENE	-	-	-	-	-	-	-
GLYOXYLIC ACID	-	120.426	-	-	-	-	-
VANILLYLMANDELIC ACID	-	-	-	-	-	-	-
CO_2	-	-	-	-	0.002	-	-
$Cu(OH)_2$	-	-	-	-	-	145.954	-
Cu_2O	-	-	-	-	-	-	-
Sodium guaiacolate	-	-	-	-	-	-	-
Na_2SO_4	-	-	-	-	-	-	-
H_2SO_4	-	-	-	-	-	-	-
Temperature (C)	**25**	**25**	**25**	**25**	**180**	**25**	**25**
Mass Flow kg/hr	**105.593**	**203.084**	**22.542**	**1498.441**	**1768.555**	**145.954**	**91.253**
Enthalpy MJ/hr	**-2.68E+02**	**-1.64E+03**	**-1.45E+02**	**-2.38E+04**	**-1.09E+04**	**1.79E+01**	**-**

Table 4-13 The mass balances simulation results of vanillin production from petrochemical pathway (Con't)

Mass Flow kg/hr	PRODS	W-VAPOR 1	LIQUID1	RLIQUID	W-Cu2O	F-H2SO4	TOEXT1
WATER	1625.952	104.766	1521.186	1516.128	5.058	0.282	1516.409
O_2	19.163	18.986	0.178	0.177	0.001	-	0.177
N_2	72.090	71.504	0.587	0.585	0.002	-	0.585
VANILLIN (l)	112.114	0.003	112.112	111.739	0.373	-	111.739
GUAIACOL	-	-	-	-	-	-	33.933
NaOH	1779.930		1779.930	1774.011	5.919	-	1774.011
VANILLIN (s)	-	-	-	-	-	-	-
BENZENE	0.016	0.016	-	-	-	-	-
GLYOXYLIC ACID	103.914	58.286	45.628	45.476	0.152	-	45.476
VANILLYLMANDELIC ACID	19.913	0.000	19.913	19.847	0.066	-	19.847
CO_2	32.431	30.758	1.673	1.667	0.006	-	1.667
$Cu(OH)_2$	2.175	0.133	2.042	2.035	0.007	-	2.035
Cu_2O	105.440		105.440		105.440	-	0.000
Sodium guaiacolate	40.784	0.711	40.074	39.940	0.133	-	0.000
Na_2SO_4	-	-	-	-	-	-	19.413
H_2SO_4	-	-	-	-	-	13.800	0.395
Temperature (C)	**95**	**95**	**95**	**30**	**30**	**25**	**30**
Mass Flow kg/hr	**3913.922**	**285.163**	**3628.760**	**3511.604**	**117.155**	**14.082**	**3525.687**
Enthalpy MJ/hr	**-3.73E+04**	**-1.73E+03**	**-3.56E+04**	**-3.60E+04**	**-2.44E+02**	**-1.16E+02**	**-3.62E+04**

Table 4-13 The mass balances simulation results of vanillin production from petrochemical pathway (Con’t)

Mass Flow kg/hr	**F-BENZENE**	**SOLVENTF**	**TOP1**	**BOTTOM1**	**F-WATER2**	**W-BOTTOM2**	**TODIST1**
WATER	-	7.106	4.667	1518.848	10.000	7.561	7.106
O_2	-	0.056	0.056	0.176	-	0.001	0.056
N_2	-	0.203	0.205	0.582	-	0.002	0.203
VANILLIN (l)	-	-	110.585	1.155	-	0.082	110.503
GUAIACOL	-	-	33.933	-	-	0.008	33.924
NaOH	-	-	5.460	1768.551	-	5.406	0.055
VANILLIN (s)	-	-	-	-	-	-	-
BENZENE	4.418	1500.000	1495.614	4.385	-	0.018	1495.595
GLYOXYLIC ACID	-	0.428	45.910	0.001	-	0.001	45.909
VANILLYLMANDELIC ACID	-	-	19.847	0.000	-	0.000	19.847
CO_2	-	1.626	1.632	1.661	-	0.006	1.626
$Cu(OH)_2$	-	-	0.006	2.029	-	0.006	-
Cu_2O	-	-	-	-	-	-	-
Sodium guaiacolate	-	-	-	-	-	-	-
Na_2SO_4	-	-	0.060	19.353	-	0.059	0.001
H_2SO_4	-	-	0.001	0.394	-	0.001	-
Temperature (C)	**25**	**38.5**	**30.2**	**33.7**	**25**	**30.2**	**30.2**
Mass Flow kg/hr	**4.418**	**1509.418**	**1717.976**	**3317.136**	**10.000**	**13.152**	**1714.824**
Enthalpy MJ/hr	**3.17E+00**	**8.58E+02**	**2.40E+02**	**-3.56E+04**	**-1.58E+02**	**-1.55E+02**	**2.37E+02**

Table 4-13 The mass balances simulation results of vanillin production from petrochemical pathway (Con't)

Mass Flow kg/hr	TODIST2	TOCOOL	TODIST3	R□GUAIACOL	R-BENZENE	R□GLYOXYLIC□ACID	F-WATER3
WATER	7.106	-	7.106	-	7.106	-	3192.000
O_2	0.056	-	0.056	-	0.056	-	-
N_2	0.203	-	0.203	-	0.203	-	-
VANILLIN (l)	-	110.503	-	-	-	-	-
GUAIACOL	33.005	0.919	-	33.005	-	-	-
NaOH	-	0.055	-	-	-	-	-
VANILLIN (s)	-	-	-	-	-	-	-
BENZENE	1495.595	-	1495.590	0.005	1495.582	0.008	-
GLYOXYLIC ACID	45.909	-	45.520	0.390	0.428	45.092	-
VANILLYLMANDELIC ACID	-	19.847	-	-	-	-	-
CO_2	1.626	-	1.626	-	1.626	-	-
$Cu(OH)_2$	-	-	-	-	-	-	-
Cu_2O	-	-	-	-	-	-	-
Sodium guaiacolate	-	-	-	-	-	-	-
Na_2SO_4	-	0.001	-	-	-	-	-
H_2SO_4	-	-	-	-	-	-	-
Temperature (C)	**41**	**288**	**39.6**	**200.2**	**38.5**	**111**	**25**
Mass Flow kg/hr	**1583.500**	**131.324**	**1550.100**	**33.400**	**1505.000**	**45.100**	**3192.000**
Enthalpy MJ/hr	**6.62E+02**	**-3.11E+02**	**7.42E+02**	**-7.07E+01**	**8.56E+02**	**-5.28E+01**	**-5.07E+04**

Table 4-13 The mass balances simulation results of vanillin production from petrochemical pathway (Con't)

Mass Flow kg/hr	TOCRYS	TOFIL	W-LIQUID	TOWASH	WETVANIL	P-VANILLIN
WATER	-	3192.000	3181.045	10.955	0.594	0.455
O_2	-	-	-	-	-	-
N_2	-	-	-	-	-	-
VANILLIN (l)	110.503	10.929	10.892	0.038	0.001	0.001
GUAIACOL	0.919	0.919	0.916	0.003	0.000	0.000
NaOH	0.055	0.055	0.054	0.000	0.000	0.000
VANILLIN (s)	-	99.574	-	99.574	99.574	99.574
BENZENE	-	-	-	-	-	-
GLYOXYLIC ACID	-	-	-	-	-	-
VANILLYLMANDELIC ACID	19.847	19.847	19.779	0.068	0.002	0.002
CO_2	-	-	-	-	-	-
$Cu(OH)_2$	-	-	-	-	-	-
Cu_2O	-	-	-	-	-	-
Sodium guaiacolate	-	-	-	-	-	-
Na_2SO_4	0.001	0.001	0.001	-	-	-
H_2SO_4	-	-	-	-	-	-
Temperature (C)	**55**	**5**	**5**	**5**	**4.7**	**5.6**
Mass Flow kg/hr	**131.324**	**3323.324**	**3212.687**	**110.637**	**100.171**	**100.032**
Enthalpy MJ/hr	**-3.72E+02**	**-5.10E+04**	**-5.09E+04**	**-1.77E+02**	**-1.16E+01**	**-9.50E+00**

From Figure 3-7 and Table 4-13, the amount of vanillin product obtained from the main reactor is 112.11 kg/hr. The product stream including vanillin, impurities unreacted raw materials, and other by-product go to separation process. The first step is flashing to remove remaining gas from the product stream. After that, copper (I) oxide that occurs in reactor is removed by solid fitter. Liquid solution from solid filter is fed to neutralization tank to convert sodium guaiacolate to guaiacol by sulfuric acid. After the neutralization, vanillin and other impurities go to the top of the first extraction column. Benzene which is used as an extraction solvent is fed at the bottom of this extraction column. The main impurities that are removed from products stream in this column are sodium hydroxide and sodium sulfate. Sodium hydroxide and sodium sulfate are separated from products stream and exits as bottom outlet of this column. This is because the solubility of sodium hydroxide and sodium sulfate in benzene are much less than the solubility of vanillin in this solvent. So, most of vanillin, some sodium hydroxide, other impurities and ethyl acetate go to the bottom of the second extraction column for remaining sodium hydroxide disposal by excess water. A next unit of the separation process is distillation column. This column separates remaining raw materials, extraction solvent and other products like guaiacol (raw material), glyoxylic acid and benzene from vanillin and other phenolic compounds like vanillylmandelic acid and remaining sodium hydroxide. The separation principle is based on different boiling temperature of each component. The lighter components go to the second and the third distillation columns to separate unreacted raw materials, and recycle back to reuse again. The benzene solvent is then separated from other components as distillate stream at the third distillation column. This distillate stream is recycled and reused as solvent in the extraction column again.

Table 4-14 Boiling temperature of all components in products stream that it is fed to first distillation column

Components	**Boiling temperature (℃)**
Sodium hydroxide	1556.85
Vanillylmandelic acid	421.33
Vanillin	284.85
Guaiacol	205
Glyoxylic acid	111
Water	100
Benzene	80

The boiling point temperature of all components in the product stream that it is fed to the first distillation column is shown in Table 4-14.

4.4 Techno-economic analysis results

The performance of vanillin production from Kraft lignin with three different separation pathways and from petrochemical pathway are compared and evaluated followed techno-economic method in this section. They are evaluated based on energy consumption, net carbon dioxide emission, and economic analysis result.

Table 4-15 Performance comparison between vanillin production from Kraft lignin with three separation pathways and petrochemical pathway

Production evaluation	**Pathway 1 (1 Extraction)**	**Pathway 2 (2 Extractions)**	**Pathway 3 (Vacuum Distillation)**	**Petrochem Vanillin**
Vanillin production rate (kg/hr)	100.033	100.032	100.033	100.032
Vanillin purity (%)	99.5	99.5	99.5	99.5
Energy evaluation				
Energy usage in reaction unit (MJ/h)	13,712.02	13,879.97	14,172.18	433.55
Energy usage in separation units (MJ/h)	77,644.17	76,898.33	266,407.15	43,853.92
Reaction: separation ratio	0.177	0.180	0.053	0.010
Energy efficiency				
Energy usage in vanillin production section (MJ/h)	91,356.18	90,778.30	280,579.33	44,287.47
Energy usage per kg of product (energy usage in vanillin production section MJ/kg of vanillin)	913.26	907.49	2,804.87	442.73
Total kg of CO_2 emission in vanillin production section	132.30	153.32	143.27	132.90
CO_2 emission per one unit of vanillin (kg/kg)	1.32	1.53	1.43	1.33
Total energy consumption (MJ/h)	**91,356.18**	**90,778.30**	**280,579.33**	**44,287.47**

4.4.1 Energy consumption

According to Table 4-15, the energy consumption of vanillin production from Kraft lignin with three separation pathways and from the petrochemical pathway are compared. The result of energy consumption of the second pathway is 907.49 MJ/kg-vanillin which is the lowest energy consumption pathway compared with the other two separation pathways. This is because two extraction units which is the main separation unit of this pathway does not requires energy. And the energy consumption of solvent evaporation unit in this pathway is relatively low compared with the other Kraft lignin pathways.

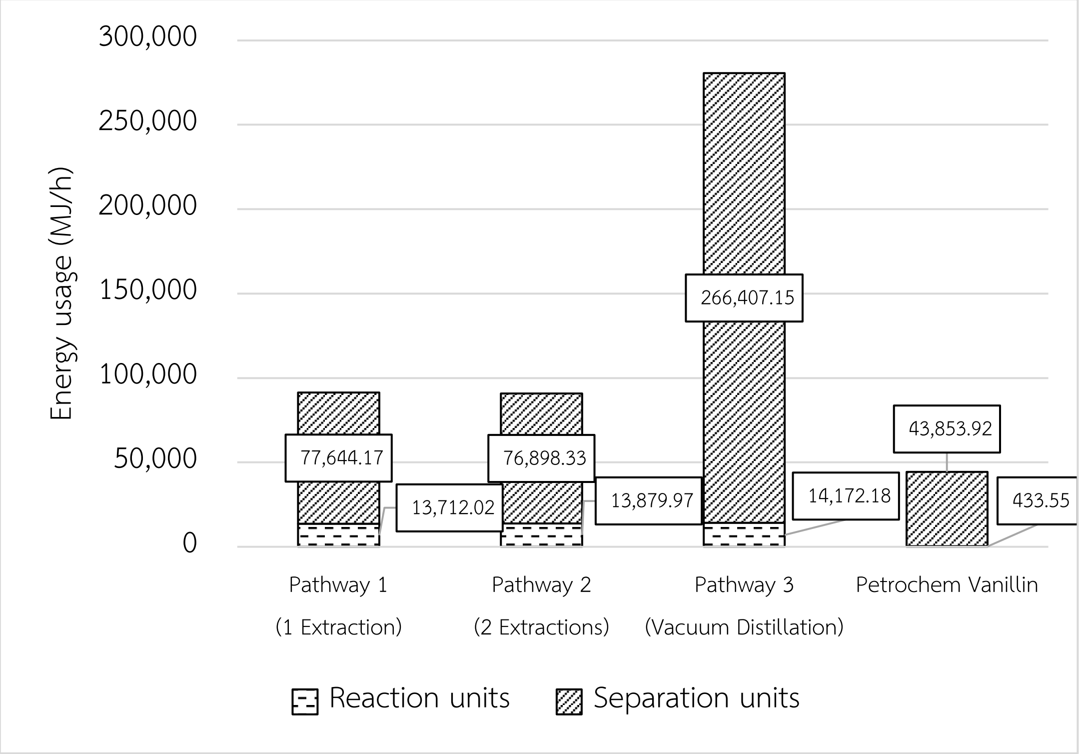


Figure 4-9 Energy consumption in reaction units and separation unit of vanillin production from Kraft lignin and petrochemical pathway

The comparison of energy consumption in reaction section and separation section of vanillin production from Kraft lignin and petrochemical pathway is shown in Figure 4-9. The first separation pathway uses slightly higher energy consumption than the second separation pathway. This is because the distillation unit in the first separation pathway is designed to remove all ethyl acetate solvent from products solution to reuse in extraction unit again. Unlike the second separation pathway, the first separation pathway used water as crystallization solvent instead of ethyl acetate. As a result, the amount of recycled ethyl acetate obtained from the distillation unit is higher than that obtained from the evaporation unit in the second separation pathway. The higher amount of recycled ethyl acetate needs a larger size of equipment and consequently needs more energy consumption.

The energy consumption of vanillin production from Kraft lignin in the third separation pathway is the highest. This is because the main separation unit of this pathway is vacuum distillation. This unit must use very high energy to separate vanillin and other phenolic compounds from sodium sulfate salt. High amount of energy is needed to vaporize vanillin and other phenolic compounds, and to compress them back to liquid again by compressor.

In conclusion, the best separation pathway for production of vanillin from Kraft lignin based on energy consumption per one kilogram of vanillin product is the second separation pathway. This pathway uses lowest energy consumption when compared with other pathways. However, it should be noted that the energy consumption of the first separation pathway is not much higher than the second separation pathway. So, the first separation pathway is a potential pathway that can be used for vanillin production from Kraft lignin as well.

If we compare the energy consumption of vanillin production from Kraft lignin pathway 2 with the petrochemical pathway, the energy consumption per one kilogram of vanillin from Kraft lignin pathway 2 is 907.49 MJ/kg-Vanillin. This is still much higher than that of the petrochemical pathway which is only 442.73 MJ/kg-Vanillin. This is simply because the product yield of petrochemical pathway is much higher than product yield of Kraft lignin pathway. So, the required amount of feed stream for Kraft lignin is much higher than that of the petrochemical pathway with the same production capacity. As a result, the size of equipment for Kraft lignin with separation pathway 2 is much bigger and this led to the higher energy consumption required. The other reason is that the impurities from Kraft lignin oxidation products were much higher than those of the petrochemical pathway. And many impurities in product stream from Kraft lignin pathway have chemical structure very close to the vanillin product. So, the energy consumption required for separation units in the Kraft lignin pathway is naturally much higher than that of the petrochemical vanillin pathway. The energy consumption requirement for the Kraft lignin pathway can be decreased by finding other separation methods that use lower energy consumption. The next research may be to study the performance of other separation methods like adsorption or membrane separation. These examples of separation methods requires lower energy consumption compared with distillation column. They could be a potential alternative to reduce the total energy consumption of the Kraft lignin pathway.

4.4.2 Net CO_2 emission

The work by Fache et al. [19] specified the possible products and by- products produced from alkaline oxidative lignin depolymerization reaction. Carbon dioxide is not specified to be product in the product stream of this reaction. With this reference, it can be assumed that the vanillin production from the Kraft lignin oxidation pathway does not generate carbon dioxide emission. However, in the case of petrochemical vanillin pathway, carbon dioxide is generated from the oxidative decarboxylation reaction in the main reactor. So, this pathway can generate carbon dioxide emission about 32.43 kg/hr to the environment.

However, we need to consider carbon dioxide emission from utilities usage in each partway. This can be done by calculation based on electricity consumption of each pathway. The formula for estimation is reported by United States Environment Protection Agency shows as below. [35]

$$Emission\ factor = 7.03 \times 10^{-4}\ metric\ ton\ CO_2\ per\ kWh\ of\ electricity$$

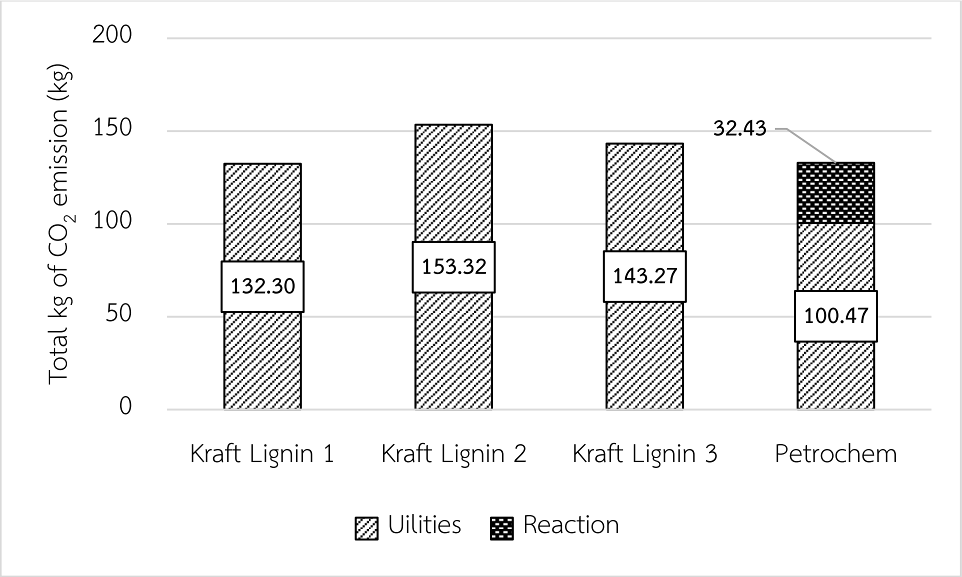


Figure 4-10 Total kg of CO_2 emission of vanillin production from Kraft lignin and petrochemical pathway

The net carbon dioxide emission of each pathway is shown in Figure 4-10. Because the carbon dioxide emission in this work is calculated from electricity consumption in the process. And it was found that all Kraft lignin pathways consumed higher electricity as compared to the petrochemical pathway. Thus, the carbon dioxide emission of all Kraft lignin pathway are higher than that of the petrochemical pathway. Although the main reaction of Kraft lignin pathway does not generate carbon dioxide emission, the utilities usage for separation units generates the carbon dioxide emission from high consumption of electricity. So, if we want to decrease the carbon dioxide emission of Kraft lignin pathway, we must find a way to decrease the electricity consumption in separation unit. If we consider carbon dioxide emission from utilities section, all Kraft lignin pathway have carbon dioxide emission higher than petrochemical pathway. But if we consider the net carbon dioxide emission from overall process including the reaction and utilities sections, the net carbon dioxide emission from the first Kraft lignin pathway is found to be slightly lower than that of the petrochemical pathway. This is because petrochemical pathway released carbon dioxide from the reaction about 32.43 kg/hr while Kraft lignin pathway releases none. So, the net carbon dioxide emission from the Kraft lignin pathway 1, which used the lowest amount of electricity, is lower than that of the petrochemical pathway. In conclusion, these three separation pathways are still not good enough to be a green pathway. The finding of other separation pathway that it used lower electricity consumption more than these three separation is interesting point to be studied.

4.4.3 Economic analysis

The economic analysis in this study is performed by using Aspen Process Economic Analyzer® version 8.8 software. The investment parameters used in this software and details of economic calculation of each simulation are shown in appendix section C. The results of economic analysis from this simulation is used to evaluate the attractiveness for investment of each Kraft lignin separation pathway. Also the economic analysis of petrochemical pathway is determined and compared.

Table 4-16 Economic analysis results of vanillin production from Kraft lignin with three separation pathways and petrochemical pathways

Cost	Pathway 1 (1 Extraction)	Pathway 2 (2 Extractions)	Pathway 3 (Vacuum Distillation)	Petrochem Vanillin
Total Capital Cost [THB]	462,683,000	448,244,000	980,083,000	620,798,000
Total Raw Materials Cost [THB/Year]	146,605,085	148,399,852	151,524,408	221,327,585
Total Chemical Used In Separation Unit Cost [THB/Year]	158,428,915	170,532,854	78,569,592	1,643,415
Total Waste Disposal Cost [THB/Year]	11,004,976	11,652,612	11,084,148	11,377,627

Table 4-16 Economic analysis results of vanillin production from Kraft lignin with three separation pathways and petrochemical pathways (Con't)

Cost	**Pathway 1 (1 Extraction)**	**Pathway 2 (2 Extractions)**	**Pathway 3 (Vacuum Distillation)**	**Petrochem Vanillin**
Total Product Sales [THB/Year]	511,966,000	511,960,013	511,966,000	511,874,000
Total Utilities Cost [THB/Year]	6,506,000	4,769,731	19,223,700	55,362,900
Total Operating Labor and Maintenance Cost [THB/Year]	12,360,000	13,000,000	24,600,000	11,120,000
P.O. Period [Year]	**6.14**	**6.43**	**7.84**	**6.18**
IRR (%)	**22.96%**	**21.87%**	**16.80%**	**23.43%**

Remark: This study used currency exchange rate is 1 USD = 31.988 THB (Currency in Aspen Process Economic Analyzer® version 8.8)

The results of economic analysis of vanillin production from Kraft lignin with three separation pathways and from the petrochemical pathways are shows in Table 4-16. The investment costs in this table are the investment cost of overall process of each simulation pathway.

Internal Rate of Return (%IRR) and Payout period (P.O. Period) are two important parameters that are used for consideration of economic analysis. The internal rate of return is the interest rate on the net present value of all cash flow from considered project equal zero. The calculation of the internal rate of return value is calculated based on avoiding the external factors such as the inflation. This factor is used to evaluate the attractiveness of the studied project. If the %IRR of that project is higher than the interest rate of loan for investment, this project is desirable. If %IRR is lower than the interest rate of loan for investment, that project should be rejected.

The Interest rate of loan in Thailand bank in 2017 is about 7% [36]. For P.O. Period factor, it shows the length of time to recover the cost of investment of considered project. If P.O. Period of considered project is longer, that project is less attractive than a project that has shorter P.O. Period.

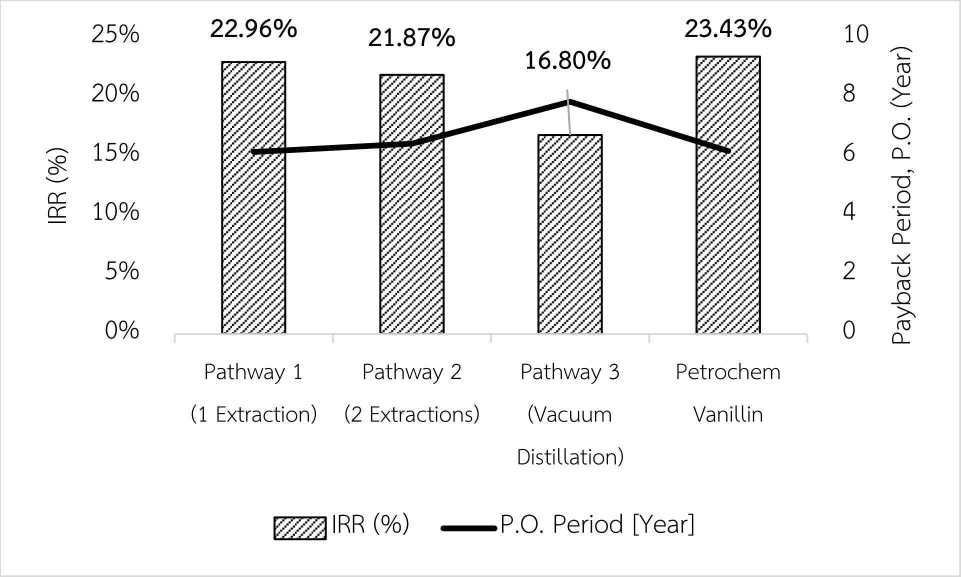


Figure 4-11 IRR (%) and payback period of vanillin production from Kraft lignin with three separation pathway and petrochemical pathway.

The economic results which include IRR (%) and payback period of vanillin production from Kraft lignin with three separation pathways and from the petrochemical pathway are shown Figure 4-11. According to Table 4-16 and Figure 4-11, the best vanillin production from the Kraft lignin pathway based on consideration of economic analysis is found to be the separation pathway 1. This pathway gives %IRR about 22.96% and payback period within 6.14 years. The separation pathway 2 gave %IRR about 21.87% and payback period of 6.43 years. These results are slightly lower than the results from the first pathway. This is because the second pathway used high amount of extraction solvent for extraction and crystallization unit. So, the cost of chemical used in separation unit is higher than that of the first pathway. In addition, it was found that waste disposal cost, labor and maintenance cost of the first pathway are lower than those of the second pathway. This is due to the smaller amount of waste that is released in the first pathway. However, utilities cost of the second pathway is lower than the first pathway. This is because the second separation pathway consumed lower energy. From above reasons, it can be seen that the economic result of the second pathway is slightly lower than the first pathway. But the IRR of the second pathway is much higher than the loan interest. So, the second pathway is attractive for investment as well as the first pathway.

For the separation pathway 3, although it gives the profit but %IRR is also lower than the separation pathway 1. This is apparently because this pathway used very high energy in separation unit. So, the utilities cost of this pathway is so high. The %IRR of this pathway is 16.80% and payout period within 7.84 years. This pathway is desirable because the %IRR is higher than the loan interest, similar to the first and the second pathway.

In conclusion, the vanillin production from Kraft lignin of the first separation pathway gives the best economic result. If we consider IRR of the first separation pathway which is 22.96%, it could be enough and desirable for investment.

However, when we compare the economic result of the Kraft lignin pathway with the result of petrochemical pathway. The %IRR of the best Kraft lignin pathway (pathway 1, %IRR = 22.96%) is still slightly lower than the %IRR of the petrochemical pathway (%IRR = 23.43%). The %IRR of petrochemical pathway is slightly higher and it is more attractive to invest than Kraft lignin pathway. This is because the vanillin production from the Kraft lignin pathway had a much lower yield of vanillin product compared with the yield obtained from the petrochemical pathway. So, the raw material feed required for the petrochemical pathway is much lower than the Kraft lignin pathway. For 100 kg/hr of vanillin production, the Kraft lignin pathway requires 1,203.64 kg/hr of feed. But for the petrochemical pathway, the required feed of guaiacol raw material is only 138.60 kg/hr. This is the big difference of required feed for the same production capacity. However, the price of raw materials used in petrochemical pathway are much higher than that of Kraft lignin pathway. The price of guaiacol is 1.5 $/kg. In comparison, Kraft lignin is a waste from pulp production process and its price is estimated to be just only 0.064 $/kg. Then, the overall raw material cost of Kraft lignin pathway is lower than the petrochemical pathway even the amount of raw material in petrochemical pathway is much higher than Kraft lignin pathway. But the main reason that makes the Kraft lignin pathway difficult to compete with the petrochemical pathway is the cost of chemical used in separation train. In case of the Kraft lignin pathway, there is large quantity of unreacted Kraft lignin left from reactor. So, the sulfuric acid used for neutralization to remove the unreacted Kraft lignin is much higher than the sulfuric acid used to convert sodium guaiacolate to guaiacol in the petrochemical pathway. Furthermore, most benzene solvent in the petrochemical pathway can be recycled and reused while some ethyl acetate solvent used in the Kraft lignin pathway is lost during the product separation and purification. So, the cost of chemical usage of the petrochemical pathway is much lower than that of the Kraft lignin pathway. Consequently, the economic result of Kraft lignin pathway is slightly lower than petrochemical pathway.

If we consider only energy consumption, carbon dioxide emission and economic analysis of vanillin production from Kraft lignin and petrochemical pathway. The petrochemical vanillin pathway shows a slightly better performance than all the Kraft lignin pathways studied. But the Kraft lignin pathway (especially pathway 1) can potentially compete with the petrochemical pathway. This is supported by the fact that the economic result of the Kraft lignin pathway was just slightly lower than the economic result of the petrochemical pathway. As mentioned earlier in chapter 1, Kraft lignin is a waste material generated from pulp and paper industry. Nowadays, Kraft lignin is typically used as a low grade energy source by burning it in a waste heat boiler in pulp production process [34]. The separation and utilization of Kraft lignin waste as raw material to produce more valuable products like vanillin is a more desirable alternative than just burning it in waste heat boiler. The economic result from this work showed that the vanillin production from Kraft lignin is attractive for investment and worth to be considered.

From the energy results, the main difference between Kraft lignin and petrochemical pathway is reaction yield of vanillin produced from these pathway. The vanillin yield from petrochemical reaction is much higher than that of the Kraft lignin oxidation reaction. One key solution to decrease energy consumption of vanillin production from Kraft lignin pathway is by improving vanillin products yield in the Kraft lignin oxidation reaction.

The second possible pathway to reduce energy consumption and improve economic result of vanillin production from Kraft lignin pathway is to find the other separation methods which use a lower amount of energy or less amount of solvent. The other possible choices of the separation pathway for next study are membrane separation and adsorption with zeolite [18]. These methods use lower energy consumption than the distillation column.

The other possible method is to find a more effective solvent. From literature, there are many choices of solvents that could be used for the liquid-liquid extraction of Kraft lignin oxidation product stream. They are, for example, chloroform, toluene, hexane, diethyl ether and ethyl acetate. Some other solvents may give better economic result than the ethyl acetate used in this study.

To sum up, the study to improve and optimize vanillin production process from Kraft lignin is very interesting. There is a good potential to make the vanillin production process from Kraft lignin competitive with commercial vanillin production from petrochemical feed. Kraft lignin is raw material from waste and it is produced in a very large amount every year. The Kraft lignin is more sustainable than petrochemical raw material like guaiacol. The petrochemical component price is depending on crude price. And petroleum crude amount is limited and has potential to run out in some day.

CHAPTER V

Conclusion

Complete simulation of vanillin production process from Kraft lignin with three different separation pathways were performed together with simulation of vanillin production process from commercial petrochemical pathway in this thesis. The simulation of complete process results can use to evaluate the possibility and attractiveness for investment of vanillin production from the Kraft lignin pathway in commercial scale.

The first section of this study dealt with the mathematic model that it is developed in the literature [6] to finding the optimal process condition for Kraft lignin oxidation, to get the best vanillin yield in the product stream. The simulation program used in this section is MATLAB® software. The optimal process conditions found from this work are 30 g/l of initial feed lignin concentration at oxygen partial pressure at 5 bars and reaction temperature of 130 °C. These condition gives vanillin yield about 9.25% of feed Kraft lignin. However, this result is still not high enough. If consider from mathematic model, vanillin yield can increase if oxygen partial pressure is increased, but this model were developed from experimental results that they studied oxygen partial pressure in range of 1.2-5 bar. So, the simulation result may not be accurate if we use the oxygen partial pressure higher than this range. The next study may be the validation of Kraft lignin oxidation model with the higher oxygen partial pressure. If we have more data on the mathematic models at higher oxygen partial pressure as well as other process conditions, a higher yield of vanillin product could be obtained.

The next part of this study is the simulation of complete vanillin production process from Kraft lignin with three separation pathways and the simulation of vanillin production process from petrochemical pathway. The simulation in this part was performed by Aspen Plus® software. The simulation contains main reaction section and separation section. The separation of vanillin from oxidation products is the important part for consideration as well. This is because Kraft lignin oxidation product stream has many components. The separation method has significant effect to final vanillin product purity. The alternative separation method is studied in this thesis contains three pathways. The best separation pathway is a liquid extraction unit followed by distillation and crystallization unit. This pathway gives vanillin final product amount 100 kg/hr (vanillin output from the reactor is 111.32 kg/hr) with 99.5% purity.

The economic analysis results of vanillin production from Kraft lignin with three separation pathways are considered and compared with the economic analysis results of the petrochemical vanillin pathway. The best Kraft lignin pathway is vanillin production from Kraft lignin with separation pathway 1. This pathway gives %IRR about 22.96% and the payout period within 6.14 years. However, this result is still slightly lower than the results from petrochemical pathway which gives %IRR about 23.43% and the payout period within 6.18 years. This is because vanillin yield of Kraft lignin oxidation reaction is much lower than the vanillin yield of petrochemical reaction. So, the required feed of raw material in Kraft lignin pathway is much higher than petrochemical pathway. So, the raw material cost of Kraft lignin pathway is not much lower than that of petrochemical pathway even the cost of Kraft lignin is much lower than the cost of guaiacol. But the remaining raw material from oxidation reaction in Kraft lignin pathway is much higher than that of petrochemical pathway. So, sulfuric acid that it is used to remove the remaining Kraft lignin in oxidation products solution is much higher than the sulfuric that it is used to convert sodium guaiacolate to guaiacol in petrochemical pathway. And benzene solvent used in the petrochemical pathway is much more effective than the ethyl acetate solvent used in the Kraft lignin pathway. So, the chemicals cost usage in the separation unit of Kraft lignin pathway is much higher than that of petrochemical pathway. If consider the %IRR and the payout period result of vanillin production from Kraft lignin with separation pathway 1, the vanillin production with this separation process is desirable to make the commercial scale. But the performance of Kraft lignin pathway is still lower than that of the petrochemical pathway. There are many options to improve the process performance. The example methods are improving vanillin yield of Kraft lignin oxidation reaction, finding other separation methods that use a lower utilities consumption, or finding other solvents for extraction in extraction column. The study about finding the method to make the vanillin production from the Kraft lignin pathway has better performance is very interesting. This is because vanillin production from the Kraft lignin pathway use more sustainable raw material than petrochemical pathway, Kraft lignin is waste from pulp and paper industry and it comes from wood (nature product) that it is the stable source more than a petrochemical raw material source. This is because the amount of crude oil is limited and price is not stable. And the separation of Kraft lignin from black liquor before feed to re-boiler in pulp production process will improve the efficiency of re-boiler [34]. So, this is another one reason to separate Kraft lignin for making vanillin by appropriate process is interesting to study.

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APPENDIX A

A1 Components mass flow rate used in simulation of vanillin production from Kraft lignin pathway by Aspen Plus® software

A.1.1 Kraft lignin pathway 1

Lignin concentration = 30 g/l (the optimum condition from section 4-2)

NaOH concentration = 40 g/l (Araújo et al. 2008)

Reaction time = 67 min (result from MATLAB® program)

= 1.117 hr.

Lignin mass flow rate = 1,203.638 kg/hr (setting)

NaOH mass flow rate = 1,203.638 kg/hr (lignin mass flow rate) X$\frac{40\,\frac{g}{l}\,[Lignin]}{30\,\frac{g}{l}\,[NaOH]}$

= 1,604.851 kg/hr

Find water mass flow rate:

Lignin feed = 1,203.638 kg/hr X 1.117 hr = 1,344.464 kg

NaOH = 1,604.851 kg/hr X 1.117 hr = 1,792.619 kg

Solution volume (V) = $\frac{Lignin\ feed\ mass}{Lignin\ concentration\ in\ solution}$

= $\frac{1{,}344.464\ X\ 10^3\ g\ of\ lignin}{30\,\frac{g}{l}\,concentration\ of\ lignin\ in\ solution}$

= 44,815 liter = 44.815 m^3

Solution volume flow rate = $\frac{44.815\ m^3}{1.117\ hr}$ = 40.121 m^3/hr

Density of solution = 1,015.544 kg/m^3 (Aspen Plus® software)

Solution mass flow rate = $1{,}015.544\,\frac{kg}{m^3} \times 40.121\ m^3/hr = 40{,}744.641\ kg/hr$

Water mass flow rate = Solution mass flow rate – Lignin mass flow rate – NaOH mass flow rate

Water mass flow rate = 40,744.641 – 1,203.638 – 1,604.851

= 37,936 kg/hr

A.1.2 Kraft lignin pathway 2

Lignin concentration = 30 g/l (the optimum condition from section 4-2)

NaOH concentration = 40 g/l (Araújo et al. 2008)

Reaction time = 64.30 min (result from MATLAB® program)

= 1.117 hr.

Lignin mass flow rate = 1,218.373 kg/hr (setting)

NaOH mass flow rate = 1,218.373 kg/hr (lignin mass flow rate) X$\frac{40\,\frac{g}{l}\,[Lignin]}{30\,\frac{g}{l}\,[NaOH]}$

= 1,624.497 kg/hr

Find water mass flow rate:

Lignin feed = 1,218.373 kg/hr X 1.117 hr = 1,360.923 kg

NaOH = 1,624.497 kg/hr X 1.117 hr = 1,814.563 kg

Solution volume (V) = $\frac{Lignin\ feed\ mass}{Lignin\ concentration\ in\ solution}$

= $\frac{1{,}360.923\ X\ 10^{3}\ g\ of\ lignin}{30\,\frac{g}{l}\ concentration\ of\ lignin\ in\ solution}$

= 45,364 liter = 45.364 m^3

Solution volume flow rate = $\frac{45.364\ m^3}{1.117\ hr}$ = 40.612 m^3/hr

Density of solution = 1,015.544 kg/m^3 (Aspen Plus® software)

Solution mass flow rate = $1{,}015.544\,\frac{kg}{m^3} \times 40.612\ m^3/hr = 41{,}243.273\ kg/hr$

Water mass flow rate = Solution mass flow rate – Lignin mass flow rate – NaOH mass flow rate

Water mass flow rate = 41,243.273 – 1,218.373 – 1,624.497

= 38,400 kg/hr

A.1.3 Kraft lignin pathway 3

Lignin concentration = 30 g/l (the optimum condition from section 4-2)

NaOH concentration = 40 g/l (Araújo et al. 2008)

Reaction time = 64.30 min (result from MATLAB® program)

= 1.117 hr.

Lignin mass flow rate = 1,244.022 kg/hr (setting)

NaOH mass flow rate = 1,244.022 kg/hr (lignin mass flow rate) X$\frac{\mathbf{40\,\frac{g}{l}\,[Lignin]}}{\mathbf{30\,\frac{g}{l}\,[NaOH]}}$

= 1,658.696 kg/hr

Find water mass flow rate:

Lignin feed = 1,244.022 kg/hr X 1.117 hr = 1,389.573 kg

NaOH = 1,658.696 kg/hr X 1.117 hr = 1,852.763 kg

Solution volume (V) = $\frac{\mathbf{Lignin\ feed\ mass}}{\mathbf{Lignin\ concentration\ in\ solution}}$

= $\frac{\mathbf{1{,}389.573\ X\ 10^3\ g\ of\ lignin}}{\mathbf{30\,\frac{g}{l}\,concentration\ of\ lignin\ in\ solution}}$

= 46,319 liter = 46.319 m^3

Solution volume flow rate = $\frac{\mathbf{46.319\ m^3}}{\mathbf{1.117\ hr}}$ = 41.467 m^3/hr

Density of solution = 1,015.544 kg/m^3 (Aspen Plus® software)

Solution mass flow rate = $\mathbf{1{,}015.544\frac{kg}{m^3} \times 41.467\ m^3/hr = 42{,}111.563\ kg/hr}$

Water mass flow rate = Solution mass flow rate – Lignin mass flow rate – NaOH mass flow rate

Water mass flow rate = 42,111.563 – 1,244.022 – 1,658.696

= 39,209 kg/hr

APPENDIX B

B1 Energy consumption of each equipment in simulation from Aspen Plus® software

B1.1 Kraft lignin pathway 1

Block	Duty [MJ/hr]	Remark
Condenser@RADFRAC1	607.147	Separation
COOLER1	1,487.695	Separation
COOLER2	981.253	Separation
COOLER3	356.392	Separation
COOLER4	0.817	Separation
FLASH1_heat_Exchanger	62,584.431	Separation
HEATER1	1.052	Separation
HEATEX2	39.180	Separation
NEUTILIZ_heat_Exchanger	10,552.321	Separation
REACTOR_heat_Exchanger	13,619.733	Reaction
Reboiler@RADFRAC1	650.726	Separation
Crystal	383.150	Separation
Dryer	0.002	Separation
Compressor	33.646	Reaction
Pump	58.641	Reaction
Total	**91,356.184**	

Utilities energy consumption

Utility	MJ/hr	Utility	MJ/hr
LP Steam	76,567.200	Air	13,581.264
MP Steam	650.612	Refrigerant 1	0.817
Total Hot Utilities	**77,217.812**	**Total Cold Utilities**	**13,582.081**

B1.2 Kraft lignin pathway 2

Block	Duty [MJ/hr]	Remark
COOLEA1	30.638	Separation
COOLER1	1,505.906	Separation
COOLER2	993.311	Separation
COOLER3	0.817	Separation
FLASH1_heat_Exchanger	63,349.517	Separation
FLASH4_heat_Exchanger	76.449	Separation
HEATER1	1.122	Separation
NEUTILIZ_heat_Exchanger	10,681.512	Separation
REACTOR_heat_Exchanger	13,786.154	Reaction
Compressor	34.594	Reaction
Crystal	247.431	Separation
Crystal 2	11.627	Separation
Dryer	4.90E-08	Separation
Pump	59.217	Reaction
Total	**90,778.295**	

Utilities energy consumption

Utility	MJ/hr	Utility	MJ/hr
LP Steam	77,194.800	Air	13,162.864
		Refrigerant 1	0.817
Total Hot Utilities	**77,194.800**	**Total Cold Utilities**	**13,163.681**

B1.3 Kraft lignin pathway 3

Block	Duty [MJ/h]	Remark
Condenser@RADFRAC1	83,637.820	Separation
COOLER1	1,537.608	Separation
COOLER2	1,014.286	Separation
COOLER3	0.817	Separation
COOLER4	628.827	Separation
EVAP_heat_Exchanger	20,943.046	Separation
FLASH1_heat_Exchanger	64,681.697	Separation
HEATER1	10.294	Separation
NEUTILIZ_heat_Exchanger	10,757.514	Separation
REACTOR_heat_Exchanger	14,075.687	Reaction
Reboiler@RADFRAC1	82,829.336	Separation
Compressor	36.269	Reaction
Crystal	363.544	Separation
Dryer	2.26E-05	Separation
Pump	60.219	Reaction
Pump 2	2.363	Separation
Total	**280,579.327**	

Utilities energy consumption

Utility	MJ/hr	Utility	MJ/hr
Fired Heat (1000)	82,843.200	Air	97,487.200
LP Steam	99,704.720	Refrigerant 1	0.817
Total Hot Utilities	**182,547.920**	**Total Cold Utilities**	**97,488.017**

B1.4 Petrochemical pathway

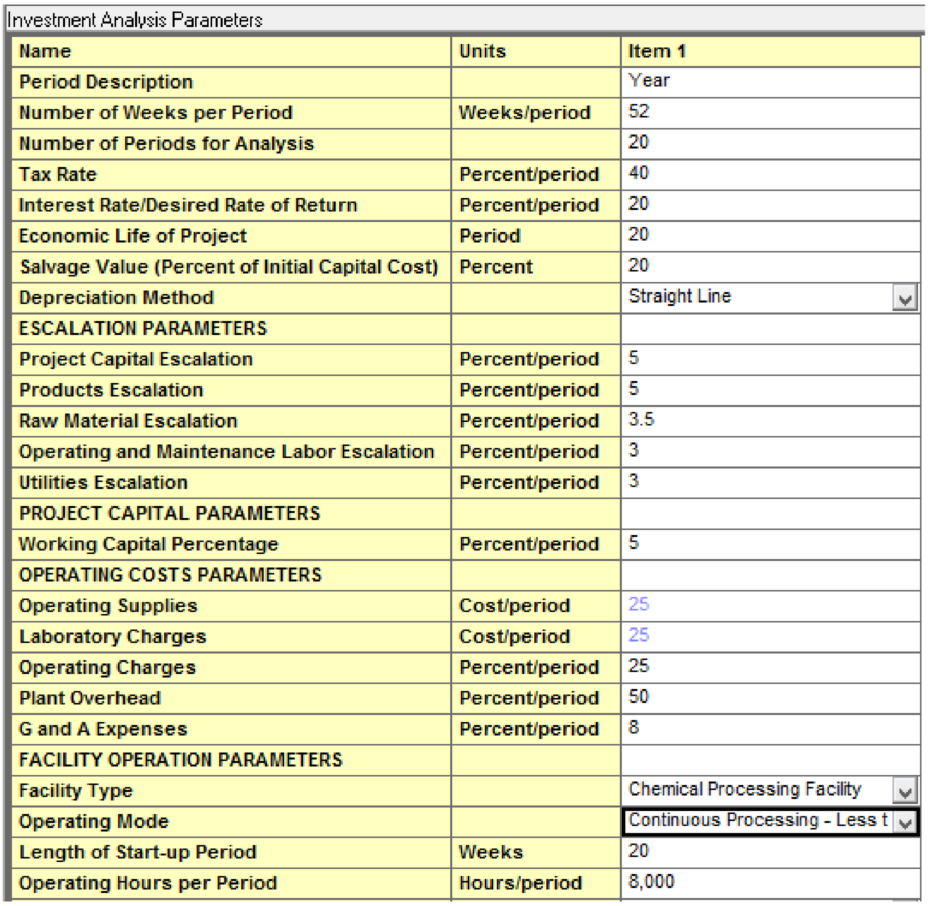
Block	Duty [MJ/hr]	Remark
EVAP_heat_Exchanger	4,304.140	Separation
HEATER1	0.206	Separation
HEATER2	339.622	Separation
HEATER3	0.479	Separation
HEATEX	60.595	Separation
Reboiler@RADFRAC1	2,659.052	Separation
Reboiler@RADFRAC2	8,441.989	Separation
Reboiler@RADFRAC3	7,926.537	Separation
Condenser@RADFRAC1	2,544.564	Separation
Condenser@RADFRAC2	8,433.195	Separation
Condenser@RADFRAC3	7,865.083	Separation
COOLER1	662.492	Separation
COOLER2	0.817	Separation
CRYSTAL	379.737	Separation
DRYER	2.71E-08	Separation
NEUTILIZ	57.412	Separation
REACTOR	433.549	Reaction
FLASH1	8.41E-12	Separation
SEP	178.002	Separation
Total	**44,287.472**	

Utilities energy consumption

Utility	MJ/hr	Utility	MJ/hr
LP Steam	8,267.584	Cooling Water	22,593.600
HP Steam	13,100.104	Air	433.462
Fired Heat (1000)	2,661.024	Refrigerant 1	0.817
Total Hot Utilities	**24,028.712**	**Total Cold Utilities**	**23,027.879**

APPENDIX C

C1 Investment parameters for calculation in Aspen Process Economic Analyzer® Version 8.8 software



Investment Analysis Parameters

Name	Units	Item 1
Period Description		Year
Number of Weeks per Period	Weeks/period	52
Number of Periods for Analysis		20
Tax Rate	Percent/period	40
Interest Rate/Desired Rate of Return	Percent/period	20
Economic Life of Project	Period	20
Salvage Value (Percent of Initial Capital Cost)	Percent	20
Depreciation Method		Straight Line
ESCALATION PARAMETERS		
Project Capital Escalation	Percent/period	5
Products Escalation	Percent/period	5
Raw Material Escalation	Percent/period	3.5
Operating and Maintenance Labor Escalation	Percent/period	3
Utilities Escalation	Percent/period	3
PROJECT CAPITAL PARAMETERS		
Working Capital Percentage	Percent/period	5
OPERATING COSTS PARAMETERS		
Operating Supplies	Cost/period	25
Laboratory Charges	Cost/period	25
Operating Charges	Percent/period	25
Plant Overhead	Percent/period	50
G and A Expenses	Percent/period	8
FACILITY OPERATION PARAMETERS		
Facility Type		Chemical Processing Facility
Operating Mode		Continuous Processing - Less t
Length of Start-up Period	Weeks	20
Operating Hours per Period	Hours/period	8,000

Labor cost

Operator level : 500 THB/day $= \dfrac{500\ THB}{8\ hrs}$ = 62.5 THB/hr

Supervisor : 2,000 THB/day $= \dfrac{2{,}000\ THB}{8\ hrs}$ = 250 THB/hr

Utilities unit costs

Electricity : 2.48 THB/kWH

Portable Water : 0 THB/ m^3

Fuel : 251.11 THB/MMBTU

Instrument Air : 0 THB/m^3

C2 Economic analysis results from Aspen Process Economic Analyzer® Version 8.8 software

C2.1 Kraft lignin pathway 1

TW (Number of Weeks per Period)	Weeks/period	52
T (Number of Periods for Analysis)	Period	20
DTEPC (Duration of EPC Phase)	Period	0.596154
DT (Duration of EPC Phase and Startup)	Period	0.980769
WORKP (Working Capital Percentage)	Percent/period	5
OPCHG (Operating Charges)	Percent/period	25
PLANTOVH (Plant Overhead)	Percent/period	50
CAPT (Total Project Cost)	Cost	4.63E+08
RAWT (Total Raw Material Cost)	Cost/period	3.05E+08
PRODT (Total Product Sales)	Cost/period	5.12E+08
OPMT (Total Operating Labor and Maintenance Cost)	Cost/period	1.24E+07
UTILT (Total Utilities Cost) **Include**d waste disposal	Cost/period	1.75E+07
ROR (Desired Rate of Return/Interest Rate)	Percent/period	20
AF (ROR Annuity Factor)		5
TAXR (Tax Rate)	Percent/period	40
IF (ROR Interest Factor)		1.2
ECONLIFE (Economic Life of Project)	Period	20
SALVAL (Salvage Value (Percent of Initial Capital Cost))	Percent	20
DEPMETH (Depreciation Method)		Straight Line
DEPMETHN (Depreciation Method Id)		1
ESCAP (Project Capital Escalation)	Percent/period	5
ESPROD (Products Escalation)	Percent/period	5
ESRAW (Raw Material Escalation)	Percent/period	3.5
ESLAB (Operating and Maintenance Labor Escalation)	Percent/period	3

ESUT (Utilities Escalation)	Percent/period	3
START (Start Period for Plant Startup)	Period	1
DESRET (Desired Return on Project for Sales Forecasting)	Percent/Period	10.5
END (End Period for Economic Life of Project)	Period	20
GA (G and A Expenses)	Percent/Period	8
DTEP (Duration of EP Phase before Start of Construction)	Period	0.192308
OP (Total Operating Labor Cost)	Cost/period	5.50E+06
MT (Total Maintenance Cost)	Cost/period	6.86E+06

Variables in result table

DEP (Depreciation Expense)

E (Earnings Before Taxes)

TAX (Taxes)

NE (Net Earnings)

TED (Total Earnings)

TEX (Total Expenses (Excludes Taxes and Depreciation))

CF (CashFlow for Project)

PV (Present Value of Cash Flows):

$$PV = \frac{CF_n}{(1+IRR)^n}$$

Where i = Period or year

IRR = Internal rate of return

NPV (Net Present Value):

$$NPV = \sum_{0}^{n} \frac{CF_n}{(1+IRR)^n} - CF_0$$

Results of vanillin production from Kraft lignin oxidation with separation pathway 1 from Aspen Process Economic Analyzer® Version 8.8 software

Year	Sales (Cost/period)	Expenses (Cost/period)					OP (Operating Costs), Cost/period					
	SP (Products Sales)	CAP (Capital Costs)	Unescalated Cumulative Capital Cost	Capital Cost	Cumulative Capital Cost	Working Capital	Raw Materials	Operating Labor Cost	Maintenance Cost	Utilities	Operating Charges	Plant Overhead
0	0	0	0	0	0	0	0	0	0	0	0	0
1	1.03E+07	5.10E+08	4.63E+08	4.86E+08	4.86E+08	2.43E+07	1.27E+08	2.29E+06	2.85E+06	7.28E+06	5.72E+05	2.57E+06
2	5.64E+08		4.63E+08		4.86E+08		3.27E+08	5.83E+06	7.28E+06	1.86E+07	1.46E+06	6.56E+06
3	5.93E+08		4.63E+08		4.86E+08		3.38E+08	6.01E+06	7.50E+06	1.91E+07	1.50E+06	6.75E+06
4	6.22E+08		4.63E+08		4.86E+08		3.50E+08	6.19E+06	7.72E+06	1.97E+07	1.55E+06	6.96E+06
5	6.53E+08		4.63E+08		4.86E+08		3.62E+08	6.38E+06	7.95E+06	2.03E+07	1.59E+06	7.16E+06
6	6.86E+08		4.63E+08		4.86E+08		3.75E+08	6.57E+06	8.19E+06	2.09E+07	1.64E+06	7.38E+06
7	7.20E+08		4.63E+08		4.86E+08		3.88E+08	6.76E+06	8.44E+06	2.15E+07	1.69E+06	7.60E+06
8	7.56E+08		4.63E+08		4.86E+08		4.02E+08	6.97E+06	8.69E+06	2.22E+07	1.74E+06	7.83E+06
9	7.94E+08		4.63E+08		4.86E+08		4.16E+08	7.18E+06	8.95E+06	2.28E+07	1.79E+06	8.06E+06
10	8.34E+08		4.63E+08		4.86E+08		4.30E+08	7.39E+06	9.22E+06	2.35E+07	1.85E+06	8.31E+06

Results of vanillin production from Kraft lignin oxidation with separation pathway 1 from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	Sales (Cost/period)	Expenses (Cost/period)					OP (Operating Costs), Cost/period					
	SP (Products Sales)	CAP (Capital Costs)	Unescalated Cumulative Capital Cost	Capital Cost	Cumulative Capital Cost	Working Capital	Raw Materials	Operating Labor Cost	Maintenance Cost	Utilities	Operating Charges	Plant Overhead
11	8.76E+08		4.63E+08		4.86E+08		4.45E+08	7.61E+06	9.50E+06	2.42E+07	1.90E+06	8.55E+06
12	9.19E+08		4.63E+08		4.86E+08		4.61E+08	7.84E+06	9.78E+06	2.50E+07	1.96E+06	8.81E+06
13	9.65E+08		4.63E+08		4.86E+08		4.77E+08	8.08E+06	1.01E+07	2.57E+07	2.02E+06	9.08E+06
14	1.01E+09		4.63E+08		4.86E+08		4.94E+08	8.32E+06	1.04E+07	2.65E+07	2.08E+06	9.35E+06
15	1.06E+09		4.63E+08		4.86E+08		5.11E+08	8.57E+06	1.07E+07	2.73E+07	2.14E+06	9.63E+06
16	1.12E+09		4.63E+08		4.86E+08		5.29E+08	8.83E+06	1.10E+07	2.81E+07	2.21E+06	9.92E+06
17	1.17E+09		4.63E+08		4.86E+08		5.47E+08	9.09E+06	1.13E+07	2.89E+07	2.27E+06	1.02E+07
18	1.23E+09		4.63E+08		4.86E+08		5.67E+08	9.36E+06	1.17E+07	2.98E+07	2.34E+06	1.05E+07
19	1.29E+09		4.63E+08		4.86E+08		5.86E+08	9.64E+06	1.20E+07	3.07E+07	2.41E+06	1.08E+07
20	1.36E+09		4.63E+08		4.86E+08		6.07E+08	9.93E+06	1.24E+07	3.16E+07	2.48E+06	1.12E+07

Results of vanillin production from Kraft lignin oxidation with separation pathway 1 from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	OP (Operating Costs), Cost/period		R (Revenue), Cost/period						Results (Cost/period)		
	Subtotal Operating Costs	G and A Costs	DEP	E	TAX	NE	TED	TEX	CF	PV	NPV
0	0	0	0	0	0	0	0	0	0	0	0
1	1.43E+08	1.14E+07	1.85E+07	-6.73E+08	0.00E+00	-6.73E+08	-6.54E+08	6.65E+08	-6.54E+08	-6.53E+08	-6.53E+08
2	3.66E+08	2.93E+07	1.85E+07	1.50E+08	6.01E+07	9.01E+07	1.09E+08	3.96E+08	1.09E+08	1.08E+08	-5.45E+08
3	3.79E+08	3.03E+07	1.85E+07	1.65E+08	6.59E+07	9.88E+07	1.17E+08	4.09E+08	1.17E+08	1.17E+08	-4.28E+08
4	3.92E+08	3.14E+07	1.85E+07	1.80E+08	7.21E+07	1.08E+08	1.27E+08	4.24E+08	1.27E+08	1.26E+08	-3.03E+08
5	4.06E+08	3.25E+07	1.85E+07	1.97E+08	7.87E+07	1.18E+08	1.37E+08	4.38E+08	1.37E+08	1.35E+08	-1.68E+08
6	4.20E+08	3.36E+07	1.85E+07	2.14E+08	8.57E+07	1.29E+08	1.47E+08	4.53E+08	1.47E+08	1.45E+08	-2.25E+07
7	4.34E+08	3.47E+07	1.85E+07	2.33E+08	9.32E+07	1.40E+08	1.58E+08	4.69E+08	1.58E+08	1.56E+08	1.33E+08
8	4.49E+08	3.59E+07	1.85E+07	2.53E+08	1.01E+08	1.52E+08	1.70E+08	4.85E+08	1.70E+08	1.67E+08	3.00E+08
9	4.65E+08	3.72E+07	1.85E+07	2.74E+08	1.10E+08	1.64E+08	1.83E+08	5.02E+08	1.83E+08	1.79E+08	4.80E+08
10	4.81E+08	3.84E+07	1.85E+07	2.96E+08	1.19E+08	1.78E+08	1.96E+08	5.19E+08	1.96E+08	1.92E+08	6.72E+08

Results of vanillin production from Kraft lignin oxidation with separation pathway 1 from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	OP (Operating Costs), Cost/period		R (Revenue), Cost/period						Results (Cost/period)		
	Subtotal Operating Costs	G and A Costs	DEP	E	TAX	NE	TED	TEX	CF	PV	NPV
11	4.97E+08	3.98E+07	1.85E+07	3.20E+08	1.28E+08	1.92E+08	2.11E+08	5.37E+08	2.11E+08	2.05E+08	8.77E+08
12	5.14E+08	4.11E+07	1.85E+07	3.45E+08	1.38E+08	2.07E+08	2.26E+08	5.55E+08	2.26E+08	2.20E+08	1.10E+09
13	5.32E+08	4.26E+07	1.85E+07	3.72E+08	1.49E+08	2.23E+08	2.42E+08	5.75E+08	2.42E+08	2.35E+08	1.33E+09
14	5.50E+08	4.40E+07	1.85E+07	4.01E+08	1.60E+08	2.40E+08	2.59E+08	5.94E+08	2.59E+08	2.51E+08	1.58E+09
15	5.69E+08	4.55E+07	1.85E+07	4.31E+08	1.72E+08	2.59E+08	2.77E+08	6.15E+08	2.77E+08	2.68E+08	1.85E+09
16	5.89E+08	4.71E+07	1.85E+07	4.63E+08	1.85E+08	2.78E+08	2.96E+08	6.36E+08	2.96E+08	2.86E+08	2.14E+09
17	6.09E+08	4.87E+07	1.85E+07	4.97E+08	1.99E+08	2.98E+08	3.17E+08	6.58E+08	3.17E+08	3.05E+08	2.44E+09
18	6.30E+08	5.04E+07	1.85E+07	5.33E+08	2.13E+08	3.20E+08	3.38E+08	6.81E+08	3.38E+08	3.25E+08	2.76E+09
19	6.52E+08	5.22E+07	1.85E+07	5.71E+08	2.28E+08	3.43E+08	3.61E+08	7.04E+08	3.61E+08	3.46E+08	3.11E+09
20	6.75E+08	5.40E+07	1.85E+07	6.11E+08	2.45E+08	3.67E+08	3.85E+08	7.29E+08	5.01E+08	4.79E+08	3.59E+09
									IRR (Internal Rate of Return)		**22.96%**
									PO (Payout Period)		**6.14**

C2.2 Kraft lignin pathway 2

TW (Number of Weeks per Period)	Weeks/period	52
T (Number of Periods for Analysis)	Period	20
DTEPC (Duration of EPC Phase)	Period	0.576923
DT (Duration of EPC Phase and Startup)	Period	0.961538
WORKP (Working Capital Percentage)	Percent/period	5
OPCHG (Operating Charges)	Percent/period	25
PLANTOVH (Plant Overhead)	Percent/period	50
CAPT (Total Project Cost)	Cost	4.48E+08
RAWT (Total Raw Material Cost)	Cost/period	3.19E+08
PRODT (Total Product Sales)	Cost/period	5.12E+08
OPMT (Total Operating Labor and Maintenance Cost)	Cost/period	1.30E+07
UTILT (Total Utilities Cost) Included waste disposal	Cost/period	1.64E+07
ROR (Desired Rate of Return/Interest Rate)	Percent/period	20
AF (ROR Annuity Factor)		5
TAXR (Tax Rate)	Percent/period	40
IF (ROR Interest Factor)		1.2
ECONLIFE (Economic Life of Project)	Period	20
SALVAL (Salvage Value (Percent of Initial Capital Cost))	Percent	20
DEPMETH (Depreciation Method)		Straight Line
DEPMETHN (Depreciation Method Id)		1
ESCAP (Project Capital Escalation)	Percent/period	5
ESPROD (Products Escalation)	Percent/period	5
ESRAW (Raw Material Escalation)	Percent/period	3.5
ESLAB (Operating and Maintenance Labor Escalation)	Percent/period	3
ESUT (Utilities Escalation)	Percent/period	3

START (Start Period for Plant Startup)	Period	1
DESRET (Desired Return on Project for Sales Forecasting)	Percent/Period	10.5
END (End Period for Economic Life of Project)	Period	20
GA (G and A Expenses)	Percent/Period	8
DTEP (Duration of EP Phase before Start of Construction)	Period	0.192308
OP (Total Operating Labor Cost)	Cost/period	6.00E+06
MT (Total Maintenance Cost)	Cost/period	7.00E+06

Variables in result table

DEP (Depreciation Expense)

E (Earnings Before Taxes)

TAX (Taxes)

NE (Net Earnings)

TED (Total Earnings)

TEX (Total Expenses (Excludes Taxes and Depreciation))

CF (CashFlow for Project)

PV (Present Value of Cash Flows):

$$PV = \frac{CF_n}{(1+IRR)^n}$$

Where i = Period or year

IRR = Internal rate of return

NPV (Net Present Value):

$$NPV = \sum_{0}^{n} \frac{CF_n}{(1+IRR)^n} - CF_0$$

Results of vanillin production from Kraft lignin oxidation with separation pathway 2 from Aspen Process Economic Analyzer® Version 8.8 software

Year	Sales (Cost/period)	Expenses (Cost/period)					OP (Operating Costs), Cost/period					
	SP (Products Sales)	CAP (Capital Costs)	Unescalated Cumulative Capital Cost	Capital Cost	Cumulative Capital Cost	Working Capital	Raw Materials	Operating Labor Cost	Maintenance Cost	Utilities	Operating Charges	Plant Overhead
0	0	0	0	0	0	0	0	0	0	0	0	0
1	2.07E+07	4.94E+08	4.48E+08	4.71E+08	4.71E+08	2.35E+07	1.40E+08	2.61E+06	3.05E+06	7.16E+06	6.54E+05	2.83E+06
2	5.64E+08		4.48E+08		4.71E+08		3.42E+08	6.37E+06	7.43E+06	1.74E+07	1.59E+06	6.90E+06
3	5.93E+08		4.48E+08		4.71E+08		3.54E+08	6.56E+06	7.65E+06	1.79E+07	1.64E+06	7.10E+06
4	6.22E+08		4.48E+08		4.71E+08		3.66E+08	6.75E+06	7.88E+06	1.85E+07	1.69E+06	7.32E+06
5	6.53E+08		4.48E+08		4.71E+08		3.79E+08	6.96E+06	8.11E+06	1.90E+07	1.74E+06	7.54E+06
6	6.86E+08		4.48E+08		4.71E+08		3.92E+08	7.16E+06	8.36E+06	1.96E+07	1.79E+06	7.76E+06
7	7.20E+08		4.48E+08		4.71E+08		4.06E+08	7.38E+06	8.61E+06	2.02E+07	1.84E+06	7.99E+06
8	7.56E+08		4.48E+08		4.71E+08		4.20E+08	7.60E+06	8.87E+06	2.08E+07	1.90E+06	8.23E+06
9	7.94E+08		4.48E+08		4.71E+08		4.35E+08	7.83E+06	9.13E+06	2.14E+07	1.96E+06	8.48E+06
10	8.34E+08		4.48E+08		4.71E+08		4.50E+08	8.06E+06	9.41E+06	2.21E+07	2.02E+06	8.74E+06

Results of vanillin production from Kraft lignin oxidation with separation pathway 2 from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	Sales (Cost/period)	Expenses (Cost/period)					OP (Operating Costs), Cost/period					
	SP (Products Sales)	CAP (Capital Costs)	Unescalated Cumulative Capital Cost	Capital Cost	Cumulative Capital Cost	Working Capital	Raw Materials	Operating Labor Cost	Maintenance Cost	Utilities	Operating Charges	Plant Overhead
11	8.76E+08		4.48E+08		4.71E+08		4.66E+08	8.31E+06	9.69E+06	2.27E+07	2.08E+06	9.00E+06
12	9.19E+08		4.48E+08		4.71E+08		4.82E+08	8.55E+06	9.98E+06	2.34E+07	2.14E+06	9.27E+06
13	9.65E+08		4.48E+08		4.71E+08		4.99E+08	8.81E+06	1.03E+07	2.41E+07	2.20E+06	9.55E+06
14	1.01E+09		4.48E+08		4.71E+08		5.16E+08	9.08E+06	1.06E+07	2.48E+07	2.27E+06	9.83E+06
15	1.06E+09		4.48E+08		4.71E+08		5.34E+08	9.35E+06	1.09E+07	2.56E+07	2.34E+06	1.01E+07
16	1.12E+09		4.48E+08		4.71E+08		5.53E+08	9.63E+06	1.12E+07	2.64E+07	2.41E+06	1.04E+07
17	1.17E+09		4.48E+08		4.71E+08		5.72E+08	9.92E+06	1.16E+07	2.71E+07	2.48E+06	1.07E+07
18	1.23E+09		4.48E+08		4.71E+08		5.92E+08	1.02E+07	1.19E+07	2.80E+07	2.55E+06	1.11E+07
19	1.29E+09		4.48E+08		4.71E+08		6.13E+08	1.05E+07	1.23E+07	2.88E+07	2.63E+06	1.14E+07
20	1.36E+09		4.48E+08		4.71E+08		6.35E+08	1.08E+07	1.26E+07	2.97E+07	2.71E+06	1.17E+07

Results of vanillin production from Kraft lignin oxidation with separation pathway 2 from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	OP (Operating Costs), Cost/period		R (Revenue), Cost/period						Results (Cost/period)		
	Subtotal Operating Costs	G and A Costs	DEP	E	TAX	NE	TED	TEX	CF	PV	NPV
0	0	0	0	0	0	0	0	0	0	0	0
1	1.56E+08	1.25E+07	1.79E+07	-6.60E+08	0.00E+00	-6.60E+08	-6.42E+08	6.63E+08	-6.42E+08	-6.41E+08	-6.41E+08
2	3.81E+08	3.05E+07	1.79E+07	1.35E+08	5.39E+07	8.08E+07	9.87E+07	4.12E+08	9.87E+07	9.83E+07	-5.42E+08
3	3.94E+08	3.16E+07	1.79E+07	1.49E+08	5.95E+07	8.92E+07	1.07E+08	4.26E+08	1.07E+08	1.06E+08	-4.36E+08
4	4.08E+08	3.26E+07	1.79E+07	1.64E+08	6.54E+07	9.82E+07	1.16E+08	4.41E+08	1.16E+08	1.15E+08	-3.21E+08
5	4.22E+08	3.38E+07	1.79E+07	1.80E+08	7.18E+07	1.08E+08	1.26E+08	4.56E+08	1.26E+08	1.24E+08	-1.96E+08
6	4.37E+08	3.49E+07	1.79E+07	1.96E+08	7.86E+07	1.18E+08	1.36E+08	4.72E+08	1.36E+08	1.34E+08	-62420944
7	4.52E+08	3.61E+07	1.79E+07	2.15E+08	8.58E+07	1.29E+08	1.47E+08	4.88E+08	1.47E+08	1.44E+08	8.20E+07
8	4.67E+08	3.74E+07	1.79E+07	2.34E+08	9.35E+07	1.40E+08	1.58E+08	5.05E+08	1.58E+08	1.55E+08	2.37E+08
9	4.84E+08	3.87E+07	1.79E+07	2.54E+08	1.02E+08	1.52E+08	1.70E+08	5.22E+08	1.70E+08	1.67E+08	4.04E+08
10	5.00E+08	4.00E+07	1.79E+07	2.76E+08	1.10E+08	1.65E+08	1.83E+08	5.40E+08	1.83E+08	1.79E+08	5.84E+08

Results of vanillin production from Kraft lignin oxidation with separation pathway 2 from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	OP (Operating Costs), Cost/period		R (Revenue), Cost/period						Results (Cost/period)		
	Subtotal Operating Costs	G and A Costs	DEP	E	TAX	NE	TED	TEX	CF	PV	NPV
11	5.17E+08	4.14E+07	1.79E+07	2.99E+08	1.20E+08	1.79E+08	1.97E+08	5.59E+08	1.97E+08	1.93E+08	7.76E+08
12	5.35E+08	4.28E+07	1.79E+07	3.23E+08	1.29E+08	1.94E+08	2.12E+08	5.78E+08	2.12E+08	2.06E+08	9.83E+08
13	5.54E+08	4.43E+07	1.79E+07	3.49E+08	1.40E+08	2.10E+08	2.28E+08	5.98E+08	2.28E+08	2.21E+08	1.20E+09
14	5.73E+08	4.58E+07	1.79E+07	3.77E+08	1.51E+08	2.26E+08	2.44E+08	6.19E+08	2.44E+08	2.37E+08	1.44E+09
15	5.93E+08	4.74E+07	1.79E+07	4.06E+08	1.63E+08	2.44E+08	2.62E+08	6.40E+08	2.62E+08	2.53E+08	1.69E+09
16	6.13E+08	4.90E+07	1.79E+07	4.37E+08	1.75E+08	2.62E+08	2.80E+08	6.62E+08	2.80E+08	2.71E+08	1.97E+09
17	6.34E+08	5.07E+07	1.79E+07	4.71E+08	1.88E+08	2.82E+08	3.00E+08	6.85E+08	3.00E+08	2.89E+08	2.25E+09
18	6.56E+08	5.25E+07	1.79E+07	5.06E+08	2.02E+08	3.03E+08	3.21E+08	7.09E+08	3.21E+08	3.09E+08	2.56E+09
19	6.79E+08	5.43E+07	1.79E+07	5.43E+08	2.17E+08	3.26E+08	3.44E+08	7.33E+08	3.44E+08	3.30E+08	2.89E+09
20	7.02E+08	5.62E+07	1.79E+07	5.82E+08	2.33E+08	3.49E+08	3.67E+08	7.58E+08	4.79E+08	4.59E+08	3.35E+09
									IRR (Internal Rate of Return)		**21.87%**
									PO (Payout Period)		**6.43**

C2.3 Kraft lignin pathway 3

TW (Number of Weeks per Period)	Weeks/period	52
T (Number of Periods for Analysis)	Period	20
DTEPC (Duration of EPC Phase)	Period	0.980769
DT (Duration of EPC Phase and Startup)	Period	1.36538
WORKP (Working Capital Percentage)	Percent/period	5
OPCHG (Operating Charges)	Percent/period	25
PLANTOVH (Plant Overhead)	Percent/period	50
CAPT (Total Project Cost)	Cost	9.80E+08
RAWT (Total Raw Material Cost)	Cost/period	2.30E+08
PRODT (Total Product Sales)	Cost/period	5.12E+08
OPMT (Total Operating Labor and Maintenance Cost)	Cost/period	2.46E+07
UTILT (Total Utilities Cost) Included waste disposal	Cost/period	3.03E+07
ROR (Desired Rate of Return/Interest Rate)	Percent/period	20
AF (ROR Annuity Factor)		5
TAXR (Tax Rate)	Percent/period	40
IF (ROR Interest Factor)		1.2
ECONLIFE (Economic Life of Project)	Period	20
SALVAL (Salvage Value (Percent of Initial Capital Cost))	Percent	20
DEPMETH (Depreciation Method)		Straight Line
DEPMETHN (Depreciation Method Id)		1
ESCAP (Project Capital Escalation)	Percent/period	5
ESPROD (Products Escalation)	Percent/period	5
ESRAW (Raw Material Escalation)	Percent/period	3.5
ESLAB (Operating and Maintenance Labor Escalation)	Percent/period	3
ESUT (Utilities Escalation)	Percent/period	3

START (Start Period for Plant Startup)	Period	1
DESRET (Desired Return on Project for Sales Forecasting)	Percent/Period	10.5
END (End Period for Economic Life of Project)	Period	20
GA (G and A Expenses)	Percent/Period	8
DTEP (Duration of EP Phase before Start of Construction)	Period	0.211538
OP (Total Operating Labor Cost)	Cost/period	5.50E+06
MT (Total Maintenance Cost)	Cost/period	1.91E+07

Variables in result table

DEP (Depreciation Expense)

E (Earnings Before Taxes)

TAX (Taxes)

NE (Net Earnings)

TED (Total Earnings)

TEX (Total Expenses (Excludes Taxes and Depreciation))

CF (Cash Flow for Project)

PV (Present Value of Cash Flows):

$$PV = \frac{CF_n}{(1+IRR)^n}$$

Where i = Period or year

IRR = Internal rate of return

NPV (Net Present Value):

$$NPV = \sum_{0}^{n} \frac{CF_n}{(1+IRR)^n} - CF_0$$

Results vanillin production from Kraft lignin oxidation with separation pathway 3 from Aspen Process Economic Analyzer® Version 8.8 software

Year	Sales (Cost/period)	Expenses (Cost/period)					OP (Operating Costs), Cost/period					
	SP (Products Sales)	CAP (Capital Costs)	Unescalated Cumulative Capital Cost	Capital Cost	Cumulative Capital Cost	Working Capital	Raw Materials	Operating Labor Cost	Maintenance Cost	Utilities	Operating Charges	Plant Overhead
0	0	0	0	0	0	0	0	0	0	0	0	0
1	0	1.08E+09	9.80E+08	1.03E+09	1.03E+09	5.15E+07	4.58E+06	1.09E+05	3.78E+05	6.00E+05	2.72E+04	2.44E+05
2	3.58E+08		9.80E+08		1.03E+09		2.46E+08	5.83E+06	2.03E+07	3.22E+07	1.46E+06	1.30E+07
3	5.93E+08		9.80E+08		1.03E+09		2.55E+08	6.01E+06	2.09E+07	3.31E+07	1.50E+06	1.34E+07
4	6.22E+08		9.80E+08		1.03E+09		2.64E+08	6.19E+06	2.15E+07	3.41E+07	1.55E+06	1.38E+07
5	6.53E+08		9.80E+08		1.03E+09		2.73E+08	6.38E+06	2.21E+07	3.51E+07	1.59E+06	1.43E+07
6	6.86E+08		9.80E+08		1.03E+09		2.83E+08	6.57E+06	2.28E+07	3.62E+07	1.64E+06	1.47E+07
7	7.20E+08		9.80E+08		1.03E+09		2.93E+08	6.76E+06	2.35E+07	3.73E+07	1.69E+06	1.51E+07
8	7.56E+08		9.80E+08		1.03E+09		3.03E+08	6.97E+06	2.42E+07	3.84E+07	1.74E+06	1.56E+07
9	7.94E+08		9.80E+08		1.03E+09		3.14E+08	7.18E+06	2.49E+07	3.95E+07	1.79E+06	1.60E+07
10	8.34E+08		9.80E+08		1.03E+09		3.25E+08	7.39E+06	2.57E+07	4.07E+07	1.85E+06	1.65E+07

Results vanillin production from Kraft lignin oxidation with separation pathway 3 from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	Sales (Cost/period)	Expenses (Cost/period)					OP (Operating Costs), Cost/period					
	SP (Products Sales)	CAP (Capital Costs)	Unescalated Cumulative Capital Cost	Capital Cost	Cumulative Capital Cost	Working Capital	Raw Materials	Operating Labor Cost	Maintenance Cost	Utilities	Operating Charges	Plant Overhead
11	8.76E+08		9.80E+08		1.03E+09		3.36E+08	7.61E+06	2.64E+07	4.20E+07	1.90E+06	1.70E+07
12	9.19E+08		9.80E+08		1.03E+09		3.48E+08	7.84E+06	2.72E+07	4.32E+07	1.96E+06	1.75E+07
13	9.65E+08		9.80E+08		1.03E+09		3.60E+08	8.08E+06	2.80E+07	4.45E+07	2.02E+06	1.81E+07
14	1.01E+09		9.80E+08		1.03E+09		3.72E+08	8.32E+06	2.89E+07	4.58E+07	2.08E+06	1.86E+07
15	1.06E+09		9.80E+08		1.03E+09		3.85E+08	8.57E+06	2.98E+07	4.72E+07	2.14E+06	1.92E+07
16	1.12E+09		9.80E+08		1.03E+09		3.99E+08	8.83E+06	3.06E+07	4.86E+07	2.21E+06	1.97E+07
17	1.17E+09		9.80E+08		1.03E+09		4.13E+08	9.09E+06	3.16E+07	5.01E+07	2.27E+06	2.03E+07
18	1.23E+09		9.80E+08		1.03E+09		4.27E+08	9.36E+06	3.25E+07	5.16E+07	2.34E+06	2.09E+07
19	1.29E+09		9.80E+08		1.03E+09		4.42E+08	9.64E+06	3.35E+07	5.31E+07	2.41E+06	2.16E+07
20	1.36E+09		9.80E+08		1.03E+09		4.58E+08	9.93E+06	3.45E+07	5.47E+07	2.48E+06	2.22E+07

Results vanillin production from Kraft lignin oxidation with separation pathway 3 from Aspen Process Economic Analyzer® Version 8.8 software (Con't)

Year	OP (Operating Costs), Cost/period		R (Revenue), Cost/period				Results (Cost/period)				
	Subtotal Operating Costs	G and A Costs	DEP	E	TAX	NE	TED	TEX	CF	PV	NPV
0	0	0	0	0	0	0	0	0	0	0	0
1	5.94E+06	4.75E+05	3.92E+07	-1.13E+09	0.00E+00	-1.13E+09	-1.09E+09	1.09E+09	-1.09E+09	-1.09E+09	-1.09E+09
2	3.19E+08	2.55E+07	3.92E+07	-2.58E+07	0.00E+00	-2.58E+07	1.34E+07	3.45E+08	1.34E+07	1.34E+07	-1.07E+09
3	3.30E+08	2.64E+07	3.92E+07	1.97E+08	7.88E+07	1.18E+08	1.57E+08	3.56E+08	1.57E+08	1.57E+08	-9.15E+08
4	3.41E+08	2.73E+07	3.92E+07	2.15E+08	8.58E+07	1.29E+08	1.68E+08	3.69E+08	1.68E+08	1.67E+08	-7.48E+08
5	3.53E+08	2.82E+07	3.92E+07	2.33E+08	9.33E+07	1.40E+08	1.79E+08	3.81E+08	1.79E+08	1.78E+08	-5.71E+08
6	3.65E+08	2.92E+07	3.92E+07	2.53E+08	1.01E+08	1.52E+08	1.91E+08	3.94E+08	1.91E+08	1.89E+08	-3.82E+08
7	3.77E+08	3.02E+07	3.92E+07	2.74E+08	1.10E+08	1.64E+08	2.04E+08	4.07E+08	2.04E+08	2.01E+08	-1.80E+08
8	3.90E+08	3.12E+07	3.92E+07	2.96E+08	1.18E+08	1.78E+08	2.17E+08	4.21E+08	2.17E+08	2.14E+08	3.36E+07
9	4.03E+08	3.22E+07	3.92E+07	3.20E+08	1.28E+08	1.92E+08	2.31E+08	4.35E+08	2.31E+08	2.28E+08	2.61E+08
10	4.17E+08	3.33E+07	3.92E+07	3.45E+08	1.38E+08	2.07E+08	2.46E+08	4.50E+08	2.46E+08	2.42E+08	5.03E+08

Results vanillin production from Kraft lignin oxidation with separation pathway 3 from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	R (Revenue), Cost/period						Results (Cost/period)				
	Subtotal Operating Costs	G and A Costs	DEP	E	TAX	NE	TED	TEX	CF	PV	NPV
11	4.31E+08	3.45E+07	3.92E+07	3.71E+08	1.48E+08	2.23E+08	2.62E+08	4.65E+08	2.62E+08	2.57E+08	7.60E+08
12	4.45E+08	3.56E+07	3.92E+07	3.99E+08	1.60E+08	2.39E+08	2.79E+08	4.81E+08	2.79E+08	2.73E+08	1.03E+09
13	4.61E+08	3.68E+07	3.92E+07	4.29E+08	1.72E+08	2.57E+08	2.96E+08	4.97E+08	2.96E+08	2.90E+08	1.32E+09
14	4.76E+08	3.81E+07	3.92E+07	4.60E+08	1.84E+08	2.76E+08	3.15E+08	5.14E+08	3.15E+08	3.08E+08	1.63E+09
15	4.92E+08	3.94E+07	3.92E+07	4.93E+08	1.97E+08	2.96E+08	3.35E+08	5.32E+08	3.35E+08	3.27E+08	1.96E+09
16	5.09E+08	4.07E+07	3.92E+07	5.29E+08	2.11E+08	3.17E+08	3.56E+08	5.50E+08	3.56E+08	3.47E+08	2.31E+09
17	5.26E+08	4.21E+07	3.92E+07	5.66E+08	2.26E+08	3.39E+08	3.79E+08	5.68E+08	3.79E+08	3.68E+08	2.67E+09
18	5.44E+08	4.35E+07	3.92E+07	6.05E+08	2.42E+08	3.63E+08	4.02E+08	5.88E+08	4.02E+08	3.90E+08	3.06E+09
19	5.63E+08	4.50E+07	3.92E+07	6.47E+08	2.59E+08	3.88E+08	4.27E+08	6.08E+08	4.27E+08	4.14E+08	3.48E+09
20	5.82E+08	4.65E+07	3.92E+07	6.91E+08	2.76E+08	4.15E+08	4.54E+08	6.28E+08	6.99E+08	6.76E+08	4.15E+09
									IRR (Internal Rate of Return)		**16.80%**
									PO (Payout Period)		**7.84**

C2.4 Petrochemical pathway

TW (Number of Weeks per Period)	Weeks/period	52
T (Number of Periods for Analysis)	Period	20
DTEPC (Duration of EPC Phase)	Period	1.05769
DT (Duration of EPC Phase and Startup)	Period	1.44231
WORKP (Working Capital Percentage)	Percent/period	5
OPCHG (Operating Charges)	Percent/period	25
PLANTOVH (Plant Overhead)	Percent/period	50
CAPT (Total Project Cost)	Cost	6.21E+08
RAWT (Total Raw Material Cost)	Cost/period	2.23E+08
PRODT (Total Product Sales)	Cost/period	5.12E+08
OPMT (Total Operating Labor and Maintenance Cost)	Cost/period	1.11E+07
UTILT (Total Utilities Cost) Included waste disposal	Cost/period	6.67E+07
ROR (Desired Rate of Return/Interest Rate)	Percent/period	20
AF (ROR Annuity Factor)		5
TAXR (Tax Rate)	Percent/period	40
IF (ROR Interest Factor)		1.2
ECONLIFE (Economic Life of Project)	Period	20
SALVAL (Salvage Value (Percent of Initial Capital Cost))	Percent	20
DEPMETH (Depreciation Method)		Straight Line
DEPMETHN (Depreciation Method Id)		1
ESCAP (Project Capital Escalation)	Percent/period	5
ESPROD (Products Escalation)	Percent/period	5
ESRAW (Raw Material Escalation)	Percent/period	3.5
ESLAB (Operating and Maintenance Labor Escalation)	Percent/period	3
ESUT (Utilities Escalation)	Percent/period	3

START (Start Period for Plant Startup)	Period	2
DESRET (Desired Return on Project for Sales Forecasting)	Percent/Period	10.5
END (End Period for Economic Life of Project)	Period	21
GA (G and A Expenses)	Percent/Period	8
DTEP (Duration of EP Phase before Start of Construction)	Period	0.557692
OP (Total Operating Labor Cost)	Cost/period	5.00E+06
MT (Total Maintenance Cost)	Cost/period	6.12E+06

Variables in result table

DEP (Depreciation Expense)

E (Earnings Before Taxes)

TAX (Taxes)

NE (Net Earnings)

TED (Total Earnings)

TEX (Total Expenses (Excludes Taxes and Depreciation))

CF (Cash Flow for Project)

PV (Present Value of Cash Flows):

$$PV = \frac{CF_n}{(1+IRR)^n}$$

Where i = Period or year

IRR = Internal rate of return

NPV (Net Present Value):

$$NPV = \sum_{0}^{n} \frac{CF_n}{(1+IRR)^n} - CF_0$$

Results of vanillin production from petrochemical pathway from Aspen Process Economic Analyzer® Version 8.8 software

Year	Sales (Cost/period)	Expenses (Cost/period)					OP (Operating Costs), Cost/period					
	SP (Products Sales)	CAP (Capital Costs)	Unescalated Cumulative Capital Cost	Capital Cost	Cumulative Capital Cost	Working Capital	Raw Materials	Operating Labor Cost	Maintenance Cost	Utilities	Operating Charges	Plant Overhead
0	0	0	0	0	0		0	0	0	0	0	0
1	0	5.94E+08	5.65E+08	5.94E+08	5.94E+08		0	0	0	0	0	0
2	3.15E+08	6.11E+07	6.21E+08	3.00E+07	6.24E+08	3.10E+07	2.25E+08	5.00E+06	6.12E+06	6.67E+07	1.25E+06	5.56E+06
3	5.93E+08		6.21E+08		6.24E+08		2.47E+08	5.46E+06	6.69E+06	7.29E+07	1.37E+06	6.08E+06
4	6.22E+08		6.21E+08		6.24E+08		2.56E+08	5.63E+06	6.89E+06	7.51E+07	1.41E+06	6.26E+06
5	6.53E+08		6.21E+08		6.24E+08		2.65E+08	5.80E+06	7.09E+06	7.74E+07	1.45E+06	6.45E+06
6	6.86E+08		6.21E+08		6.24E+08		2.74E+08	5.97E+06	7.31E+06	7.97E+07	1.49E+06	6.64E+06
7	7.20E+08		6.21E+08		6.24E+08		2.84E+08	6.15E+06	7.53E+06	8.21E+07	1.54E+06	6.84E+06
8	7.56E+08		6.21E+08		6.24E+08		2.94E+08	6.33E+06	7.75E+06	8.45E+07	1.58E+06	7.04E+06
9	7.94E+08		6.21E+08		6.24E+08		3.04E+08	6.52E+06	7.99E+06	8.71E+07	1.63E+06	7.25E+06
10	8.34E+08		6.21E+08		6.24E+08		3.15E+08	6.72E+06	8.22E+06	8.97E+07	1.68E+06	7.47E+06

Results of vanillin production from petrochemical pathway from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	Sales (Cost/period)	Expenses (Cost/period)					OP (Operating Costs), Cost/period					
	SP (Products Sales)	CAP (Capital Costs)	Unescalated Cumulative Capital Cost	Capital Cost	Cumulative Capital Cost	Working Capital	Raw Materials	Operating Labor Cost	Maintenance Cost	Utilities	Operating Charges	Plant Overhead
11	8.75E+08		6.21E+08		6.24E+08		3.26E+08	6.92E+06	8.47E+06	9.24E+07	1.73E+06	7.70E+06
12	9.19E+08		6.21E+08		6.24E+08		3.37E+08	7.13E+06	8.73E+06	9.52E+07	1.78E+06	7.93E+06
13	9.65E+08		6.21E+08		6.24E+08		3.49E+08	7.34E+06	8.99E+06	9.80E+07	1.84E+06	8.17E+06
14	1.01E+09		6.21E+08		6.24E+08		3.61E+08	7.56E+06	9.26E+06	1.01E+08	1.89E+06	8.41E+06
15	1.06E+09		6.21E+08		6.24E+08		3.74E+08	7.79E+06	9.53E+06	1.04E+08	1.95E+06	8.66E+06
16	1.12E+09		6.21E+08		6.24E+08		3.87E+08	8.02E+06	9.82E+06	1.07E+08	2.01E+06	8.92E+06
17	1.17E+09		6.21E+08		6.24E+08		4.00E+08	8.26E+06	1.01E+07	1.10E+08	2.07E+06	9.19E+06
18	1.23E+09		6.21E+08		6.24E+08		4.14E+08	8.51E+06	1.04E+07	1.14E+08	2.13E+06	9.47E+06
19	1.29E+09		6.21E+08		6.24E+08		4.29E+08	8.77E+06	1.07E+07	1.17E+08	2.19E+06	9.75E+06
20	1.36E+09		6.21E+08		6.24E+08		4.44E+08	9.03E+06	1.11E+07	1.21E+08	2.26E+06	1.00E+07

Results of vanillin production from petrochemical pathway from Aspen Process Economic Analyzer® Version 8.8 software (Con't)

Year	OP (Operating Costs), Cost/period		R (Revenue), Cost/period						Results (Cost/period)		
	Subtotal Operating Costs	G and A Costs	DEP	E	TAX	NE	TED	TEX	**CF**	**PV**	**NPV**
0	0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	-5.94E+08	0.00E+00	-5.94E+08	-5.94E+08	5.94E+08	-5.94E+08	-5.92E+08	-5.92E+08
2	3.10E+08	2.48E+07	2.48E+07	-1.06E+08	0.00E+00	-1.06E+08	-8.08E+07	3.96E+08	-8.08E+07	-8.05E+07	-6.73E+08
3	3.40E+08	2.72E+07	2.48E+07	2.01E+08	8.03E+07	1.20E+08	1.45E+08	3.67E+08	1.45E+08	1.44E+08	-5.28E+08
4	3.51E+08	2.81E+07	2.48E+07	2.18E+08	8.72E+07	1.31E+08	1.56E+08	3.79E+08	1.56E+08	1.54E+08	-3.74E+08
5	3.63E+08	2.90E+07	2.48E+07	2.36E+08	9.46E+07	1.42E+08	1.67E+08	3.92E+08	1.67E+08	1.65E+08	-2.09E+08
6	3.75E+08	3.00E+07	2.48E+07	2.56E+08	1.02E+08	1.54E+08	1.78E+08	4.05E+08	1.78E+08	1.76E+08	-3.34E+07
7	3.88E+08	3.10E+07	2.48E+07	2.77E+08	1.11E+08	1.66E+08	1.91E+08	4.19E+08	1.91E+08	1.88E+08	1.54E+08
8	4.01E+08	3.21E+07	2.48E+07	2.99E+08	1.19E+08	1.79E+08	2.04E+08	4.33E+08	2.04E+08	2.00E+08	3.54E+08
9	4.14E+08	3.31E+07	2.48E+07	3.22E+08	1.29E+08	1.93E+08	2.18E+08	4.48E+08	2.18E+08	2.13E+08	5.68E+08
10	4.28E+08	3.43E+07	2.48E+07	3.46E+08	1.39E+08	2.08E+08	2.33E+08	4.63E+08	2.33E+08	2.27E+08	7.95E+08

Results of vanillin production from petrochemical pathway from Aspen Process Economic Analyzer® Version 8.8 software (Con’t)

Year	OP (Operating Costs), Cost/period				R (Revenue), Cost/period					Results (Cost/period)	
	Subtotal Operating Costs	G and A Costs	DEP	E	TAX	NE	TED	TEX	**CF**	**PV**	**NPV**
11	4.43E+08	3.54E+07	2.48E+07	3.72E+08	1.49E+08	2.23E+08	2.48E+08	4.78E+08	2.48E+08	2.42E+08	1.04E+09
12	4.58E+08	3.66E+07	2.48E+07	4.00E+08	1.60E+08	2.40E+08	2.65E+08	4.94E+08	2.65E+08	2.58E+08	1.29E+09
13	4.73E+08	3.78E+07	2.48E+07	4.29E+08	1.72E+08	2.58E+08	2.83E+08	5.11E+08	2.83E+08	2.74E+08	1.57E+09
14	4.89E+08	3.91E+07	2.48E+07	4.61E+08	1.84E+08	2.76E+08	3.01E+08	5.28E+08	3.01E+08	2.91E+08	1.86E+09
15	5.05E+08	4.04E+07	2.48E+07	4.93E+08	1.97E+08	2.96E+08	3.21E+08	5.46E+08	3.21E+08	3.10E+08	2.17E+09
16	5.22E+08	4.18E+07	2.48E+07	5.28E+08	2.11E+08	3.17E+08	3.42E+08	5.64E+08	3.42E+08	3.29E+08	2.50E+09
17	5.40E+08	4.32E+07	2.48E+07	5.65E+08	2.26E+08	3.39E+08	3.64E+08	5.83E+08	3.64E+08	3.50E+08	2.85E+09
18	5.58E+08	4.47E+07	2.48E+07	6.04E+08	2.42E+08	3.62E+08	3.87E+08	6.03E+08	3.87E+08	3.71E+08	3.22E+09
19	5.77E+08	4.62E+07	2.48E+07	6.45E+08	2.58E+08	3.87E+08	4.12E+08	6.23E+08	4.12E+08	3.94E+08	3.61E+09
20	5.97E+08	4.77E+07	2.48E+07	6.89E+08	2.76E+08	4.13E+08	4.38E+08	6.44E+08	4.38E+08	4.18E+08	4.03E+09
									IRR (Internal Rate of Return)		**23.43%**
									PO (Payout Period)		**6.18**

C3 Waste disposal cost of vanillin production from Kraft lignin and petrochemical pathway

C3.1 Kraft lignin pathway 1

Oxidized lignin was sold to be fuel according cost as below

Black liquor mean heating value (MJ/Kg) = 14.5 MJ/Kg [37]
Coal (wet basis) high heating value (MJ/Kg) = 14 MJ/Kg
(Source Coal India Limited)
Coal price ($/ton) = 10.06 $/ton
= 321.72 THB/ton
= 0.322 THB/Kg

Waste water treatment cost formula (Source Amata Nakorn Industrial estate)

$$TC = \left(1000 + 7.00Vi + \frac{9.41ViSi}{1000}\right) + Cp$$

Where

TC = Cost for waste water (THB/month)
Vi = Waste water volume from factory (80% of water usage)
Si = BOD of waste water (mg/l)
Cp = Penalty in case BOD is over from standard

Waste disposal cost of vanillin production from Kraft lignin with separation pathway 1

Stream	W-VAPOR1	W-SOLID	W-BOT1	W-LIQUID	W-WATER
WATER	27772.71	84.297	10859.539	3156.939	20.018
OXYGEN	2.004	0	0.001	0	0
VANILLIN	0.136	0.855	0	10.809	0.035
NITROGEN	160.228	0	0.039	0	0
VANILLIC ACID	0.566	0.236	0	30.341	0.099
SYRINGALDEHYDE	3.734	0.036	0	4.64	0.015
SO_2	6.598	0.001	0.088	0	0
ACETOVANILLONE	0.05	0.592	0	76.134	0.248
p-Hydroxybenzaldehyde	0.001	0.046	0	5.951	0.019
NaOH	0	0	0.007	0	0
ETHYL ACETATE	0	0	452.118	0.359	0.001
Na_2SO_4	0	21.925	2821.484	6.239	0.02
LIGNIN	0	129.857	0	0	0
OXIDIZED LIGNIN	0	842.04	0	0	0
Mass Flow TOTAL kg/hr	27946.027	1079.885	14133.276	3291.412	20.455
Total m3/hr	136.758		16.671	13.655	0.054
Cost THB / year	11253524.040		1382356.200	1134441.000	16438.800
Cost THB /kg		-0.322			
Cost THB/hr		-347.723			
Total waste disposal expense THB/year			11,004,976.280		

Waste disposal cost of vanillin production from Kraft lignin with separation pathway 2

Stream	W-VAPOR1	W-SOLID	W-BOTTOM1	W-BOTTOM2	W-LIQ	W-WATER
WATER	28109.865	85.336	10991.026	38.845	17.966	10.737
OXYGEN	1.810	0	0	0	0	0
VANILLIN	0.137	0.866	0	0.479	10.858	0.795
NITROGEN	161.373	0	0.039	0	0	0
VANILLIC ACID	0.573	0.239	0	0	29.508	1.271
SYRINGALDEHYDE	3.782	0.037	0	0	4.511	0.194
SO2	6.679	0.001	0.089	0	0	0
ACETOVANILLONE	0.051	0.599	0	0.075	73.974	3.186
p-Hydroxybenzaldehyde	0.001	0.047	0	0.022	5.767	0.248
NaOH	0	0	0.040	0	0.	0
ETHYL ACETATE	0	0	457.149	0.226	55.022	4.029
Na2SO4	0	22.188	2856.045	6.300	0.023	0.001
LIGNIN	0	131.449	0	0	0	0
OXIDIZED LIGNIN	0	852.367	0	0	0	0
Total kg/hr	**28284.271**	**1093.129**	**14304.388**	**45.947**	**197.629**	**20.461**
Total m3/hr	**137.523**		**16.871**	**0.052**		**0.021**
Cost THB / month	**943032.550**		**116566.350**	**1356.200**		**1143.850**
Cost THB / year	**11316390.600**		**1398796.200**	**16274.400**		**13726.200**
Cost THB /kg		**-0.322**			**1.090**	
Cost THB/hr		**-351.988**			**215.416**	**0.000**
Total waste disposal expense THB/year			**11,652,611.976**			

Waste disposal cost of vanillin production from Kraft lignin with separation pathway 3

Stream	W-VAPOR1	W-SOLID	W-BOTTOM	W-STEAM	W-LIQUID	W-WATER
WATER	28703.401	87.214	0	8088.548	3127.746	20.317
OXYGEN	1.999	0	0	0.001	0	0
VANILLIN	0.14	0.886	3.749	0.123	10.585	0.036
NITROGEN	165.332	0	0	0.04	0	0
VANILLIC ACID	0.585	0.244	31.463	0	0	0
SYRINGALDEHYDE	3.86	0.037	4.779	0.032	0	0
SO_2	6.819	0.001	0	0.09	0.001	0
ACETO-01	0.052	0.613	46.679	0.019	32.141	0.109
P-HYD-01	0.001	0.048	6.171	0	0.001	0
NaOH	0	0.175	22.473	0	0	0
Na_2SO_4	0	22.393	2882.685	0	0	0
LIGNIN	0	134.214	0	0	0.00E+00	0
OXIDIZED LIGNIN	0	870.292	0	0	0	0
Total kg/hr	28882.189	1116.117	2997.999	8088.853	3170.474	20.462
Total m3/hr	141.044		4.720	8.138	3.123	0.020
Cost THB / month	967154.140		33332.000	56745.156	22392.550	1137.000
Cost THB / year	11605849.680		1390118.875	680941.874	268710.600	13644.000
Cost THB /kg	0.480	-0.322				
Cost THB/hr		-359.390				
Total waste disposal expense THB/year	11,084,147.636					

C3.4 Petrochemical pathway

Chemical waste disposal cost used in this study (Source Waste & Resources Action Programme Company)

Liquid chemical waste disposal = 25 £/ton
= 1.09 THB/kg
Solid cake waste disposal by landfill (Hazardous) = 29 £/ton
= 1.26 THB/kg

Remark: 1 £ = 43.45 THB [Exchange rate on Jul 2017]

The waste disposal cost of vanillin production from petrochemical pathway shows in table as below

Waste disposal cost of vanillin production from petrochemical pathway

Stream	W-VAPOR1	W-Cu2O	W-VAPOR2	W-LIQ1	W-BOTTOM2	W-LIQUID	W-WATER
WATER	104.766	5.058	1430.268	88.579	7.561	3181.045	20.360
O_2	18.986	0.001	0.176	0	0.001	0	0
N_2	71.504	0.002	0.582	0	0.002	0	0
VANILLIN	0.003	0.373	0.059	1.096	0.082	10.892	0.036
GUAIACOL	0	0	0	0	0.008	0.916	0.003
NaOH	0	5.919	0	0	5.406	0.054	0
BENZENE	0.016	0	4.383	0	0.018	0	0
GLYOXYLIC ACID	58.286	0.152	0.001	0	0.001	0	0
VANILLYLMANDELIC ACID	0	0.066	0	0	0.000	19.779	0.066
CO_2	30.758	0.006	1.660	0	0.006	0	0
$Cu(OH)_2$	0.133	0.007	1.910	0.118	0.006	0	0
Cu_2O	0	105.440	0	0	0	0	0
Sodium Guaiacolate	0.711	0.133	0	0	0	0	0
Na_2SO_4	0	0	0	19.353	0.059	0.001	0
H_2SO_4	0	0	0.010	0.385	0.001	0	0
Total kg/hr	**285.163**	**117.157**	**1439.049**	**109.531**	**13.151**	**3212.687**	**20.465**
Total m3/hr	**118.369**		**1.446**	**0.122**	**0.012**	**3.202**	**0.020**
Cost THB / year	**9741956.460**		**130884.627**	**22008.935**	**12986.400**	**275204.400**	**13644.000**
Cost THB /kg		**1.260**					
Cost THB/hr		**147.618**					
Total waste disposal expense THB/year				**11,377,627.382**			

VITA

Nawaporn Khwangaisakun was born in Suphanburi province, Thailand. Monday 21st August 1989.

After she finished high school “U-Thong school” in 2008, she selected Chemical Engineering department in the faculty of Science at Chulalongkorn University and studied in 2008-2012. After she graduated the bachelor degree in 2012, she started to work with M-Wave Marketing Company Limited.

After 2 years in this company, she contacted Prof. Suttichai for studying further in M.Eng. (Chemical Engineering) at Chulalongkorn University. Prof. Suttichai is her thesis advisor and Asst. Prof. Suksun from King Mongkut's University of Technology North Bangkok, Thailand is her co-thesis advisor. She learnt a lot of knowledge and got many kind advice from them.

Finally, for 3 years of Mater Degree life, she got many lessons to use in her life.