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Purification of Lactic Acid Using Alkaline Precipitation Followed by Reactive Distillation

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***Abstrak*—** Lactic acid (LA) can be applied commercially in the biodegradable polymer industry. The production of PLA biopolymers requires lactic acid with pure isomers as its raw material, therefore the process of producing lactic acid through biological fermentation pathways is preferred over through chemical synthesis processes that produce mixed (racemic) lactic acid. In general, lactic acid purification process is carried out by several methods including precipitation and distillation. Precipitation is a conventional method for separating fermented lactic acid which is carried out through 2 stages, namely neutralization and acidification. In the process of neutralizing the fermented solution, base is added to precipitate specific lactic acid and then an acidification process is carried out by adding acid to take back the precipitated lactic acid. Distillation of a raw fermented mixture can produce very pure LA. This is an effective method for separating LA from other organic acids. The reactive distillation process is a chemical process in which the chemical reaction and the distillation process are carried out in one unit. In reactive distillation, LA forms esters with alcohols in the presence of an acid catalyst. Esters have much lower boiling points than LA. Therefore, separation can be achieved by distillation. In this research, the lactic acid purification process was carried out by combining the precipitation process

***Kata Kunci*—** Alkaline precipitation, Reactive distillation, Lactic acid, Ethanol

I. Introduction

Lactic acid (LA) is a carboxylic acid with the molecular formula ($CH_3CHOHCOOH$). Lactic acid has two isomeric forms, namely L (+) or D (-) lactic acid, which is an organic acid that belongs to multifunctional acids and is often used in the cosmetic, food, chemical and pharmaceutical industries. Lactic acid can be applied commercially in the biodegradable polymer industry. Given its wide use, it is hoped that through this research a lactic acid industry in Indonesia can be developed. Lactic acid can be made from various sources that contain carbohydrates. Various types of plants or agricultural waste containing cellulose can be used as raw material for lactic acid. production of environmentally friendly PLA (Poly Lactic Acid) biopolymers. PLA can be degraded by nature for 6 months - 2 years, much faster than polystyrene (PS) and polyethylene (PE) which take 500-1000 years for the process of degradation by the environment. The production of PLA requires lactic acid with pure isomers as its raw material, therefore the process of producing lactic acid through biological fermentation pathways is preferred over through chemical synthesis processes that produce mixed (racemic) lactic acid.

The separation process is a process that is commonly carried out in the purification process. Precipitation is a conventional method to separate lactic acid from fermentation. Precipitation is carried out in 2 stages, namely neutralization and acidification. In the process of neutralizing the fermented solution, bases such as $Ca(OH)_2$ are added; NaOH and KOH to precipitate specific lactic acid. Furthermore, the acidification process is carried out by adding acids such as sulfuric acid to take back the precipitated lactic acid.

Distillation of a raw fermented mixture can produce very pure LA. This is an effective method for separating LA from other organic acids. The reactive distillation process is a chemical process in which the chemical reaction and the distillation process are carried out in one unit. In reactive distillation, LA forms esters with lower alcohols such as methanol and ethanol with an acid catalyst. Esters have much lower boiling points than LA. Therefore, separation can be achieved by distillation.
Seo et al. studied the effect of operational variables, such as catalyst concentration, reactant-lactic acid:methanol mole ratio, feed concentration, type of alcohol (methanol, ethanol and 2-propanol) and partial condenser temperature, on yield. The yield of lactic acid obtained reached 90%. In addition, the yield of lactic acid will increase with the increase in the concentration of the catalyst in the esterification section and the mole ratio of the reactants and the concentration of lactic acid in the feed decreases [1]. In addition, Kumar et al. studied the effect of catalyst charge, mole-lactic acid : methanol ratio, boil-up rate, and feed concentration. The experimental results

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indicated that the yield of lactic acid was not affected by the catalyst load under the conditions studied, and, at low mole ratios, high yields of lactic acid were achieved [2]. The gain of lactic acid increases with increasing heat load. The recovery rate for bait with a concentration of 10% is greater than for bait with a concentration of 20% in the initial period. However, at higher feed concentrations (40%), the recovery rate of lactic acid is much higher.

The conventional purification process chosen is precipitation. Use calcium hydroxide, sodium hydroxide and ammonium hydroxide because they can separate lactic acid from the mixture and can be washed to obtain lactic acid recovery. The other method uses reactive distillation using ethanol. Because there are many processes for separating lactic acid, it is necessary to optimize the purification process in order to produce maximum lactic acid. This research has an update on the optimization of the separation process using 2 different separation methods. This research can be developed and used for industries that utilize lactic acid as a raw material.

II. MATERIALS AND METHODS

A. Materials

The material is the result of synthesis which is equated with the conditions of previous studies in the form of a 24% concentration of lactic acid solution. $Ca(OH)_2$, NH_4OH and NaOH for precipitation and ethanol for reactive distillation.

B. Research Procedures

B.1. Fermentation Process

Fermentation was carried out for 48 hours at 37°C and pH 6. Operating temperature of 37°C is the optimum temperature for lactic acid production using Lactobacillus culture. Previous studies also stated that at temperatures below 30°C and above 40°C, the product formation speed was quite slow. pH 5.5-6.5 is the optimum pH for lactic acid fermentation with Lactobacillus culture. $CaCO_3$ as much as 2 g/L is added.

B.2. Precipitation of acid with bases

The pH is controlled automatically at 6.0 using one of three basic suspensions or solutions (25% w/v): $Ca(OH)_2$, NH_4OH and NaOH. The temperature and speed of agitation were controlled at 40°C and 150 rpm, respectively. For recovery, the precipitate was washed with sulfuric acid. Then the evaporation process is carried out to reduce the water content.

B.3. Reactive distillation with ethanol

The dilute lactic acid solution mixed with ethanol and catalyst is fed into a batch distillation column system equipped with a condenser and reboiler. column was operated at total reflux for 2 hours. After that, the reflux ratio was set to 0. Most of the ethanol and water came out as distillate. While in the residue, most of it contains lactic acid, ethyl lactate and sulfuric acid. This residue is then fed back into the distillation column system and added to the dilute lactic acid solution for the hydrolysis stage. Hydrolysis is carried out with a certain reflux ratio. Hydrolysis carried out within 4 hours and a temperature of 900°C. The distillate products are ethanol and water, while lactic acid is obtained from the residue. In the esterification stage, the concentration of ethyl lactate in the residue was measured, while in the hydraulic stage, the concentration of lactic acid in the residue was measured. The flowchart diagram of lactic acid purification is shown in Figure 1.

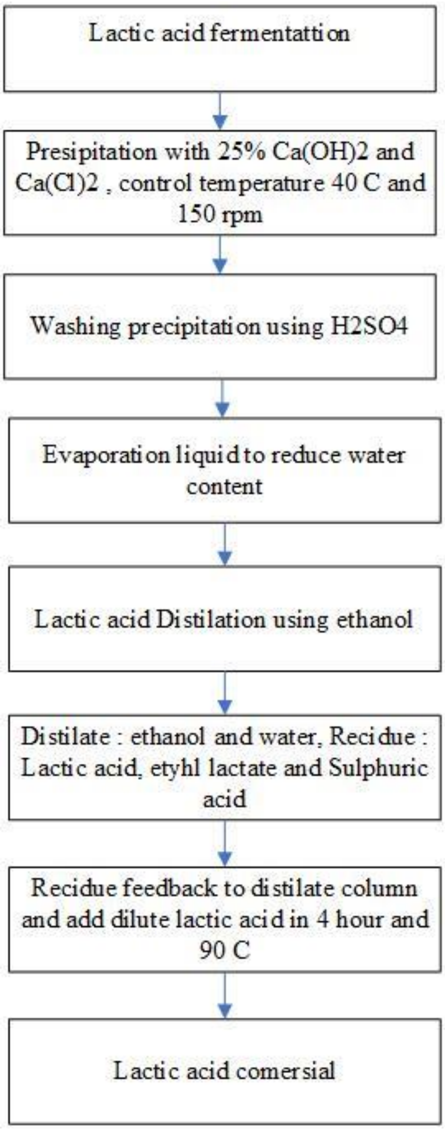

Figure 1. Flowchart diagram of lactic acid purification

B.4. Characterization

A metric alkali titration test was carried out using 1 M NaOH to determine lactic acid levels.

III. RESULTS AND DISCUSSION

A. Fermentation using *Lactobacillus*

Fermentation was carried out for 48 hours at 37°C and pH 6. Based on previous research, it was stated that an operating temperature of 37°C is the optimum temperature for lactic acid production using Lactobacillus culture. Previous studies also stated that at temperatures below

30°C and above 40°C, the product formation speed was quite slow. pH 5.5-6.5 is the optimum pH for lactic acid fermentation with Lactobacillus culture. $CaCO_3$ of 2 g/L was added as a neutralizing agent to help maintain pH during the fermentation process. The concentration of hydrogen ions in the medium has the maximum effect on microbial growth. pH affects at least two aspects of the microbial cell, namely the functioning of enzymes and the transport of nutrients into the cell. This limits the synthesis of the metabolic enzymes responsible for the synthesis of new protoplasm, and also the pH value affects the synthesis of RNA and protein [10]. During the fermentation process, DNS analysis was carried out to test the reduction in reducing sugars by taking samples every 8 hours. The decrease in reducing sugar during 48 hours of fermentation with various microorganisms *Lactobacillus rhamnosus + brevis* and *Lactobacillus delbrueckii* can be seen in Figure 2.

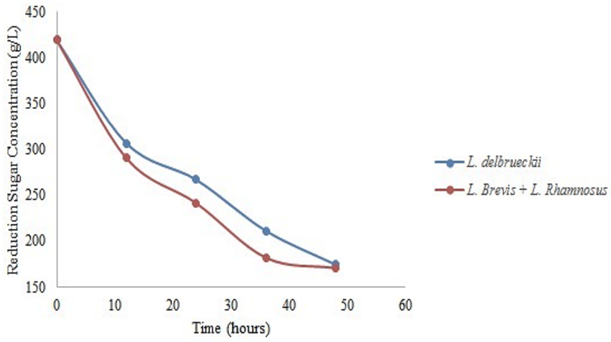

Figure 2. Graph of Fermentation Reducing Sugar Analysis

Lactobacillus delbrueckii decreased by 4.5305 g/L while the *Lactobacillus rhamnosus + Lactobacillus brevis* mixture decreased by 7.5718 g/L. This indicates that there is activity of microorganisms in the fermentation medium in the fermentation process which forms a product in the form of lactic acid. Based on the results of the study, the smallest reduction in reducing sugars was found in the use of a single *Lactobacillus delbrueckii* bacterium. This is in accordance with research of Cui et al. that the use of a mixture of microorganisms can convert reducing sugars from the substrate more efficiently when compared to using a single microorganism [3]. With a decrease in the concentration of reducing sugars in the substrate, it indicates that the microorganisms used in the fermentation process consume the existing glucose to be converted into the desired product, namely lactic acid.

TABLE 1.
RESULTS OF CALCULATION OF LACTIC ACID CONCENTRATION THROUGH THE HPLC METHOD

Bacterium Type	Lactic acid Concentration (%)
Lactobacillus delbrueckii	24.595
Lactobacillus rhamnosus + Lactobacillus brevis	24.975

From Table 1. it can be seen that the lactic acid concentration from the HPLC analysis showed the best results from the microorganism variable in the mixed culture L. rhamnosus + L. brevis with the lactic acid concentration obtained at 24.975%. Through the EMP pathway under anaerobic conditions with a maximum conversion of lactic acid of 2 mol from 1 mol of glucose [4]. This is in line with research of Cui et al. that the production of lactic acid from corn cobs using a mixed culture of L. rhamnosus + L. brevis and comparing it to a single culture obtained the highest concentration using a mixed culture of L. rhamnosus + L. brevis [3].

B. Precipitation of lactic acid with bases

The precipitation process is a more efficient purification process for fermented lactic acid. In this method excess metal hydroxide is added to the fermentation reactor to neutralize the acid produced, maintain the pH between 5.0 – 6.0 and produce metal acid salts. Administration of metal hydroxide prevents the inhibitory effect of high concentrations of lactic acid with low pH on cell metabolism [5].

In this study, the results obtained from the concentration of lactic acid in precipitation using the base $CaOH_2$; NaOH and KOH are respectively 5.3; 4.8; 4.35 mL in 20 mL. The results of precipitation with $CaOH_2$ showed a higher concentration of lactic acid compared to NaOH and KOH which is also in line with that reported by Nakao et al. The results of the concentration of lactic acid from the use of $Ca(OH)_2$ as a precipitant are higher because bivalent cations from Ca^{2+} have neutralization effectiveness against bacterial culture compared to monovalent cations from Na^+ and K^+ [5]. The reaction mechanism of the purification process is shown in Figure 3 [6].

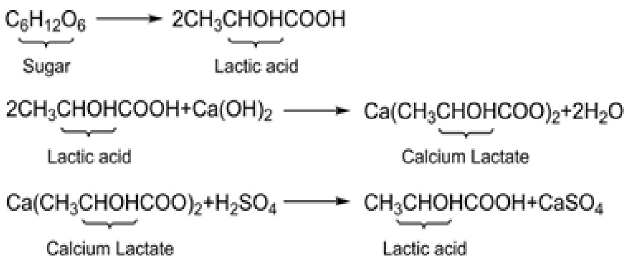

Figure 3. Mechanism of lactic acid purification [6].

Apart from the cation valence factor, the solubility value of lactate metals (calcium lactate, sodium lactate, and potassium lactate) also affects the concentration of lactic acid precipitated. The solubility value of calcium lactate is low, which is around 92.5 g/L at 40° C. The solution causes more calcium lactate in the precipitation process to precipitate so that in the washing process with sulfuric acid, more lactic acid is obtained [7]. This solubility value has a large difference with sodium lactate and potassium lactate, which ranges from 851 g/L and 786 g/L at 25° C.

Furthermore, the three precipitates formed were washed (aquadest) and precipitated with the help of a centrifugator until they reached a clear 20 mL solution. Purification using precipitation is emphasized to separate lactic acid from impurities so that in the reactive distillation process a higher purity of lactic acid is obtained.

C. Reactive Distillation

Conventional distillation at normal temperature and pressure is not efficient to obtain lactic acid from crude lactic acid. Therefore, crude lactic acid can be converted into esters before being hydrolyzed to lactic acid by a reactive distillation unit. The advantage of this method is the purification of lactic acid with high purity and efficiency.

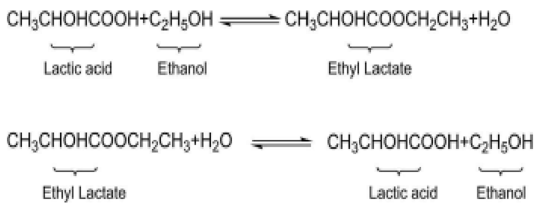

Figure 4. Reactive distillation mechanism [6].

In this study, ethanol was chosen as a lactic acid esterification agent in reactive distillation of ethanol because it was obtained from renewable resources [8]. The solution resulting from the precipitation is distilled by reactive distillation with successive levels of lactic acid in the residue with the base $CaOH_2$; NaOH and KOH are together 89.07%; 84.21; and 80.56%.

Kumar et. al. studied the continuous esterification and hydrolysis process of LA in a continuously stirred tank. The methyl lactate was completely hydrolyzed. LA is obtained from the bottom of the tower, while methanol is obtained from the top [2]. This process can be used continuously to produce very pure LA. About 85% lactate conversion and 80% LA yield was obtained experimentally. Komesu et al. investigated the interaction between different reactive distillation conditions and the optimal conditions for LA purification using a factorial experimental design [9]. Nearly 100% yield of ethyl lactate was obtained under the following conditions: ethanol/LA molar ratio was 18.4, boiling point was 125 °C, catalyst loading was 6%. After reactive distillation, the concentration of LA is three times higher than the original concentration, showing good results.

IV. Conclusion

The results of the lactic acid purification process using alkaline precipitation followed by reactive distillation using 3 catalyst variables namely $Ca(OH)_2$, NaOH, and KOH respectively: 89.07% ; 84.21% ; and 80.56 %. In this study the base $Ca(OH)_2$ gave the highest purification results compared to KOH and NaOH due to the greater cation valence and the lowest solubility of $Ca(OH)_2$ with lactic acid so that the lactic acid precipitated during the precipitation process was more.

Acknowledgement

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