Fuel Grade Bioethanol Production from Suweg Starch Through Distillation-Adsorption Process Using Natural Zeolite

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Abstract. Suweg (Amorphophallus campanulatus) is a sweet tuber which has starch content around 77%, it is suitable as raw material for fuel grade bioethanol production. Bioethanol is ethanol derived from biomass. Fuel grade bioethanol must have a minimum concentration 99.5%. This research will study the effect of zeolite adsorbent concentration on the ethanol purification. The manufacture of fuel grade bioethanol through hydrolysis, fermentation, and purification via distillation and adsorption. Hydrolysis and fermentation (SSF) were carried out on Suweg starch at concentration of 250 g/L using Stargen™ 002 at a concentration of 1.5% (w/w) and a concentration of 5 g/L Saccharomyces cerevisiae for 78 hours, producing maximum crude ethanol at a concentration of 14.09% for 54 hours. Furthermore, this crude ethanol is purified using two-stage distillation for 105 minutes and adsorption using natural zeolite with various concentration of 30-90% (w/v) for 120 minutes. The best results of distillation purification produce ethanol concentration of 94.78% (v/v) for 90 minutes, while the adsorption process stage produces 99.62% bioethanol using 90% (w/v) zeolite for 90 minutes.

1. Introduction

Starch is an important source of carbon. The large market demand and very wide industrial applications make starch as vital product. Starch also has several derivative products such as maltose, dextrin, maltodextrin, glucose, fructose, and so on which are important in the industrial world. [1]. Suweg yam (Amorphophallus campanulatus B) is one of tubers that is widely found in Indonesia, especially in Sumatra and Java. [2]. Starch content in suweg is quite high, around 77%, so it has the potential to be used as raw material for bioethanol [3].

Bioethanol is derived from biomass such as glucose, sucrose, lignocellulose and starch that is processed through hydrolysis and fermentation process [4]. Bioethanol fuel grade is bioethanol that has processed through the separation and purification stages. As fuel grade, the concentration of bioethanol should be higher than 99% [5]. Minimum ethanol content in fuel grade bioethanol is 99.5% [6]. Separation process is used to separate ethanol fermentation product from the water via distillation. However, maximum concentration of ethanol that reached by distillation only 95% due to azeotropic condition [5]. Purification process is used to increase ethanol concentration from 95% up to be higher than 99%. Kusmiyati and Susanto [5] reported that purification process using zeolite 3A as adsorbent can produced bioethanol 99%. Abdeen et al. [7] had proven that the fabricated adsorber bed apparatus has successfully used the zeolite material several times with a periodic regeneration step after each adsorption step and could produced bioethanol up to 99.5%.

The aim of this research is to study the effect of zeolite adsorbent concentration on bioethanol production from Suweg starch using Stargen™ 002 enzyme and Saccharomyces cerevisiae as yeast. Hydrolysis and fermentation were carried out simultaneously using the Simultanous Saccharification and Fermentation (SSF) method. Product will be purified using two-stages distillation and adsorption using natural zeolite.
2. Experimental
Suweg yam was obtained from Sukorejo village, Gunungpati District, Semarang City, Central Java, Indonesia. The method of starch extraction used in this study was the same as the previous method used by Hargono [3]. Natural zeolite was obtained from Klaten Regency from UD. Indrasari supplier, Semarang. The natural zeolite fraction used was zeolite with size of 2.00-2.36 mm.

2.1. Hydrolysis and Fermentation
Hydrolysis and fermentation were carried out simultaneously using the SSF method. This process was carried out in a bioreactor. Suweg starch with a concentration of 250 g/L was dissolved in distilled water. Then the pH was adjusted to 4.5 using 3M NaOH solution. The reactor which containing slurry sterilized using an autoclave at temperature of 121ºC for 30 minutes. The fermentation medium was equipped with nutrients such as (NH4)2HPO4 0.5 g/L, MgSO4.7H2O 0.025 g/L, yeast extract 1 g/L. The experiment was started by adding the Stargen™ 002 1.5% w / w and allowed to stand for 24 hours at 50ºC. The temperature was lowered to 30ºC and 5 g/L of *Saccharomyces cerevisiae* was added. The experiment was run for 78 hours and then samples were taken every 6 hours. The samples were then analyzed for glucose concentration and ethanol concentration [2].

2.2. Distillation Purification
Ethanol that was produced from the SSF process was purified using two-stages distillation methods. The first stage of ethanol is heated in boiler-1 at temperature of 78ºC to form an ethanol-water mixture vapor. The ethanol-water mixture vapor was condensed for 15-90 minutes in a condenser column filled with water as a coolant and is equipped with a spiral pipe cooler. Each time interval of 15 minutes the sample was analyzed for the concentration of ethanol using HPLC. The best ethanol yield from stage one is put into boiler-2 and heated to a temperature of 78ºC as feed for second stage distillation. The second stage was carried out in the condenser column which contains packing material for a period of time from 6,12,18 to 78 hours. The ethanol output from the condenser column was the main result of distillation processes. Analysis of the ethanol concentration from the second distillation was carried out using HPLC.

2.3. Zeolite Activation
Natural zeolite in the form of chunks was size reduced using Hammer Mill, then the zeolite grains were sieved until they pass 100 mesh sieve. This physical activation is carried out by inserting 300 g of zeolite into furnace at temperature of 200ºC for 2 hours. Furthermore, zeolite powder is cooled using air and put in a desiccator [8].

2.4. Adsorption Purification
The best result of ethanol from a two-stages distillation process was then purified using an adsorption process with a tools arrangement as shown in Figure 1. Ethanol as much as 250 mL was put into a boiling flask (A), then boiled until ethanol become a vapour so that dehydration operation occurs. Natural zeolite with mass percentage variations of 30, 60, 90 % (w / v) was placed in the packing column (B) with a diameter of 1 in and a height of 60 cm. The ethanol vapor that passes through the packing column is then condensed using a leibig cooler (C) to be accumulated in the erlenmeyer. The adsorption operation run for 120 minutes. Ethanol samples were analyzed in the first 30 minutes and after intervals of 15 minutes until 120 minutes. The samples were analyzed using HPLC to determine the ethanol concentration.
3. Results and Discussion

3.1. Effect of Fermentation Time (SSF) on Glucose Concentration and Ethanol Concentration

Experiments were carried out using raw materials of suweg starch with a concentration of 250 g/L. Process was carried out in batch condition using reactor with a volume of 1.2 L. The operation was carried out at 30°C and pH 4 for 78 hours. Data on glucose concentration and ethanol concentration are presented in Table 1.

Table 1. The Effect of Fermentation Time (SSF) on Glucose Concentration and Ethanol Concentration at Suweg Concentrations of 250 g/L, 30 °C and pH 4

| Time, h | C_{glucose}, g/L | C_{ethanol}, g/L | C_{ethanol}, % (v/v) |
|---------|------------------|------------------|----------------------|
| 0       | 0                | 0                | 0                    |
| 6       | 40.13            | 35.50            | 4.93                 |
| 12      | 65.77            | 54.62            | 7.58                 |
| 18      | 59.64            | 67.04            | 9.31                 |
| 24      | 24.40            | 78.73            | 10.93                |
| 30      | 17.09            | 89.37            | 12.41                |
| 36      | 16.41            | 96.65            | 13.42                |
| 42      | 14.82            | 100.43           | 13.94                |
| 48      | 11.71            | 101.48           | 14.09                |
| 54      | 11.53            | 101.51           | 14.09                |
| 60      | 6.70             | 101.54           | 14.10                |
| 66      | 6.70             | 101.56           | 14.10                |
| 72      | 6.70             | 101.56           | 14.10                |
| 78      | 6.70             | 101.56           | 14.10                |
Based on Table 1, the glucose concentration increased from 0 to 12 hours, reaching a concentration of 65.77 g/L. This is due to the action of enzymes in hydrolyzing starch to produce glucose [9]. Then the glucose concentration has decreased until the time of 60 hours and after that tends to be constant. The decrease in glucose concentration was caused of the consumption of yeast which converts glucose to ethanol [10]. Meanwhile, the ethanol concentration increased during the fermentation process and tended to be constant at 60 hours with a concentration of 14.10% (v/v). Huang et al. [11] reported in their study of producing bioethanol from sago hampas via SSF method resulted in bioethanol concentration of 79.65 g/L.

3.2. Effect of Distillation Time on Ethanol Concentration

The experiment was carried out in two stages. In the first stage, the best fermented ethanol is distilled for 105 minutes at 78°C. Sample was then analyzed and the analysis data were presented in Table 2.

Table 2. Effect of First Stage Distillation Time on Ethanol Concentration

| Time, Min | Ethanol Concentration, % |
|-----------|--------------------------|
| 0         | 14.10                    |
| 15        | 18.65                    |
| 30        | 22.45                    |
| 45        | 25.84                    |
| 60        | 27.98                    |
| 75        | 34.42                    |
| 90        | 36.78                    |
| 105       | 36.94                    |

The first stage distillation process was carried out using fermented ethanol at a concentration of 14.10% (v/v). Ethanol concentration increased from 15 to 90 minutes with a concentration from 18.65 up to 36.78 % (v/v). At the time of 105 minutes, ethanol concentration only increased slightly or tends to constant at concentration of 36.94% (v/v). In the first stage, the condensation of the ethanol-water mixture was carried out without using packing so that the concentration achieved were not too high. Ethanol with a concentration of 36.94% (v/v) was then continued to the second stage distillation process. Experiments were carried out for 120 minutes at 78°C as shown in Table 3.

Table 3. Effect of Second Stage Distillation Time on Ethanol Concentration

| Time, min | Ethanol Concentration, % |
|-----------|--------------------------|
| 0         | 36.94                    |
| 60        | 85.28                    |
| 75        | 88.22                    |
| 90        | 91.78                    |
| 105       | 91.80                    |
| 120       | 91.82                    |

The second stage distillation process was carried out using ethanol from the first stage distillation. There was a significant increase of ethanol concentration up to 85.28% (v/v) at 60 min. Then the concentration increased up to 91.80% (v/v) at 105 minutes. Ethanol concentration tended to be constant at 120 minutes, at concentration of 91.82% (v/v). The use of packing column was able to increase the ethanol concentration due to the longer inter-phase contact time [12]. The distillation process cannot increase the concentration even higher due to the azeotrope point between the ethanol and water mixture [13].
3.3. Effect of Zeolite Mass on Ethanol Concentration

The adsorption process was carried out in tools arrangement as shown in Figure 1. Two stages distilled ethanol in at concentration of 91.82% (v/v) was used as feed. Experiments were carried out using variable of zeolite adsorbent mass percentage of 30, 60, 90% (w/v). Operation was carried out for 120 min and it was analyzed every 15 minutes after 30 min. Analyzed data are shown in Table 4.

Table 4. Effect of Zeolite Mass on Ethanol Concentration

| Time, min | Adsorbent mass percentage, % (w/v) | Ethanol Concentration, % (v/v) |
|-----------|------------------------------------|--------------------------------|
| 0         |                                    | 91.82                          |
| 30        |                                    | 92.28                          |
| 45        |                                    | 93.02                          |
| 60        |                                    | 93.35                          |
| 75        | 30                                 | 93.98                          |
| 90        |                                    | 94.62                          |
| 105       |                                    | 94.64                          |
| 120       |                                    | 94.62                          |
| 0         |                                    | 91.82                          |
| 30        |                                    | 92.18                          |
| 45        |                                    | 93.22                          |
| 60        | 60                                 | 94.78                          |
| 75        |                                    | 95.35                          |
| 90        |                                    | 97.12                          |
| 105       |                                    | 97.14                          |
| 120       |                                    | 97.15                          |
| 0         |                                    | 91.82                          |
| 30        |                                    | 92.28                          |
| 45        |                                    | 93.22                          |
| 60        | 90                                 | 94.78                          |
| 75        |                                    | 96.35                          |
| 90        |                                    | 99.52                          |
| 105       |                                    | 99.54                          |
| 120       |                                    | 99.54                          |

At the same adsorbent mass percentage, during the increase of adsorption time, ethanol concentration obtained also increased. The ethanol concentration increases from 30 to 90 minutes then tends to be constant from 105 to 120 minutes. The increase in concentration is due to the large number of active zeolites that can absorb water. The longer the active side of the zeolite will reach its saturation point so that it cannot absorb water anymore [14]. On the other hand, at a time of 120 minutes with the adsorbent mass percentage of 30; 60; 90% (w/v) produced ethanol concentration of 94.62; 97.15; 99.54% (v/v), respectively. Handrian et al. [15] reported in their research on the adsorption of ethanol-water mixture using zeolite adsorbent resulted in ethanol concentration of 99.40%.

4. Conclusion

Adsorption of fuel grade bioethanol from suwag starch using zeolite has been studied. The best fermentation results were obtained at 60 hours with an ethanol concentration of 14.10% (v/v). The two-stage distillation yielded an ethanol concentration of 91.82% (v/v) at 120 minutes. The best percentage of zeolite adsorbent mass at 90% (w/v) produced ethanol concentration of 99.54% at 120 minutes.
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