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Fuel GradeBioethanolProduction from *Iles-iles* (*Amorphophaluscampanulatus*) Tuber

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Abstract

Fuel grade bioethanol production as an alternative fuel is desirable to substitute fossil fuel as diminishing energy source from petroleum. Bioethanol production from *Iles-iles* (*Amorphophaluscampanulatus*) tuber as alternative fuel has been conducted by hydrolysis followed by fermentation. The purification of bioethanol product was performed by distillation (using traditional and automatic distillation) and either adsorption or pervaporation. In hydrolysis process, 140 g/L of reducing sugar was produced, which then was fermented by using yeast *Sacharomycescerevisiae* (2.5-20 g/L) resulting 50-80 g/L ethanol with the concentration was 7-9% (v/v). In order to obtain 90 L ethanol with 90% purity, traditional distillation equipment required 21 hours operation, whereas automatic distillation required 12.5 hours. Then, adsorption process produced bioethanol 99% with ethanol raw materials at concentrations of 90% and 95% which resulted the breakthrough time of 60 and 120 minutes, respectively. Purification process with membrane pervaporation for 2 hours using ethanol raw material 95% (v/v) produced ethanol 99% (v/v) with ethanol flux was 20 kg/m^2.hour.

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Keywords: Fuel grade, bioethanol, hydrolysis, fermentation, adsorption, membrane pervaporation

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1. Introduction

BekonangSukoharjo Central Java, Indonesia is known as center of bioethanol small industry. Many bioethanol home industries, which produce bioethanol 100-400 L/day, are found in that area. However, the bioethanol product concentration are still very low, i.e. 30%. Only few bioethanol home industries can produce bioethanol for industrial grade, namely 70-90% v/v. Many problems are found by these home industries such as labor, technology, capital, basic material and marketing. Generally, the production process still uses simple equipment such as drum for refining, wood for cooking and other manual tools. The constraints with basic material also are faced, i.e. highly dependent on expensive and scarce molasses basic material [1].

The prospect of bioethanol use into alternative fuel is open widely because bioethanol can be used for vehicle fuel. The utilization of fuel grade bioethanol as alternative fuel is desirable to reduce dependency on petroleum and to meet the ever increasing energy consumption as well [2]. It is supported by Indonesian Government's policy that has released President Instruction, Number 1 year 2006, about biofuel use policy. Development of small industry for production of fuel grade bioethanol has several advantages, i.e., the location can close to the user, less large demand for material so that it can be built close to farm, small and affordable investment cost for small employer [2,3,4,5].

In bioethanol production, basic material is an important factor because it affects the production cost impacting to bioethanol price. To suppress bioethanol production cost, the basic material cost should be less than 40% of production cost [4,5]. The basic material used so far is molasses because the molasses processing into bioethanol use the briefest process compared with other basic material. However, the dependency on molasses basic material leads to more expensive price and less availability. Other basic materials existing in Indonesia is cassava (*Manihotutilissima Pohl*). There are other tuber and starched basic materials such as corn, potato, and sweet potato. Unfortunately, all of those materials are food material sources. In addition, the farm waste, biomass, containing cellulose and hemicelluloses can also be used including sugarcane stem, corn stem, rice straw and saw powder, and other plant waste [2,3]. Nevertheless, the processing of biomass basic material into bioethanol requires complicated technologies leading to expensive price of bioethanol [4]. Therefore, other basic materials which are nonfood resources and relatively easy to be processed into bioethanol are needed. *Iles-iles* (*Amorphophaluscampanulatus*) tuber, which grows widely in Central Java is one of the alternatives basic material [6]. It is because the availability of *Iles-iles* tuber, high carbohydrate content, and low price. It has not also been widely used for other applications.

In order to be used as fuel, the concentration of bioethanol should be higher than 99%. In this regard bioethanol product from fermentation process is purified by distillation. However, the highest concentration of ethanol than can be achieved by distillation is 95% due to azeotropic condition. Increasing concentration of ethanol from 95 to more than 99% can be performed by extraction distillation, but its operating cost is high because it requires large chemical substance and energy. For that reason, a more economic process is required. Adsorption with zeolite 3A is one of alternatives used widely in industry. Many studies showed that zeolite 3A has good productivity and selectivity for mixed ethanol-water adsorption process (e.g. [7]). Membrane pervaporation also currently becomes an attractive technology in this application. Its advantages include energy efficient, environment friendly, low operating cost, and high selectivity [8]. The objective of this study is to integrate the production process of bioethanol from *Iiles-iles* tuber through liquefaction process, enzymatic saccharification and fermentation with purification processes. The performance of traditional and automatic distillation was compared. Further, the adsorption process and membrane processes to increase bioethanol concentration higher than 95% were evaluated.

2. Method

The experiment used in this work describes in Fig. 1.

2.1. Sacharomycescerevisiae enzyme

Sacharomycescerevisiae enzyme with the capacity of 10 L/production was prepared for fermentation. The pure breed of S. *cerevisiae* (Mauripan) was bred in sterilized oblique agar (peptone, glucose, yeast media; PGY) at 121^{o}C and 1 bar for 15 minutes. PGY media was prepared by mixing extract yeast, peptone, malt and agar diluted in aqueduct. The breed stock was incubated for 2-3 days at 28^{o}C. *Sacharomycescerevisiae* from breed stock was then inoculated into pre-culture liquid media containing (NH)KH_2PO_4, $MgSO_4$.7HO, extract yeast. The pre-culture breed

was inoculated in rotary shaker at 150 rpm and temperature of 30°C for 24 hours. The process similar to pre-culture proliferation was conducted to breed main culture with twice volume larger of liquid media. The enzyme produced was used for fermentation process. All the chemical substance used had high purity (pa) from Merck.

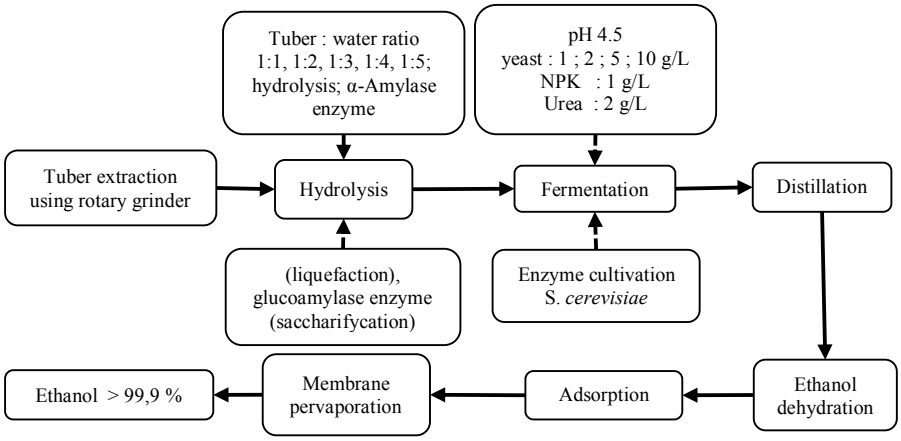

Fig 1.Flowchart of fuel grade bioethanol production process from *Iles-iles* tuber

2.2. Hydrolysis

Semi-automatic hydrolyser tank (diameter x heigh = 80 cm x 150 cm) made of stainless steel equipped with mixer, heating stove, cooler heat exchanger (diameter x heigh= 60 cm x 120 cm) and temperature adjuster was used. Fifty gram of fine powder of *Iles-iles* tuber was put into hydrolyser to which 150 L of water was added (tuber-to-water ratio = 1:3). Powder solution was mixed at 100 rpm and heated at 95°C followed by addition of 20 mL alpha-amylase enzyme (Optimax 4060 VHP, Genecor). The liquefaction process was conducted for an hour and then the temperature was decreased into 60°C using water cooler flow centrifuged in heat exchanger. Then, saccharification process was conducted on the liquefaction product solution with 20 mL gluco-amylase (AA Clearflo, Genecor). This process was lasted for 4 hours. Thereafter, the temperature was lowered to 35°C to make the solution ready to be fermented. The resulting syrup wasfiltered to separate the solid from the liquid forms before fermentation process.

2.3. Fermentation

One hundred liter solution of *Iles-iles* tuber hydrolysis product was put into fermentation tank (diameter x heigh = 60 cm x 120 cm). ThepH was adjusted to 4.5 and 10% (v/v) main culture yeast with pre-culture concentration variation containing 1, 2, 5, 10 g/L yeast was added. Then 1 g/L NPK, 2 g/L UREA as nutrition were also aded to the fermentation tank. The solution was fermented for 72 hours in loosely closed condition to keep carbon dioxide leaving. Every certain time interval (24, 48, 56, 72 hours) the fermented liquid was sampled with tape and the ethanol concentration was analyzed. After 72 hours, the fermented solution was filtered to separate the solid from the liquid forms.

2.4. Distillation

The semi-automatic distillation system made of stainless steel consisted of evaporator tank (diameter x heigh= 60 cm x 120 cm), distillation column (diameter x heigh= 20 cm x 200 cm), and condenser (diameter x heigh= 15 cm x 150 cm), heating stove, distillate reservoir (diameter x heigh= 50 cm x 50 cm), and automatic temperature adjuster. Meanwhile the traditional distillation system consisted of evaporator drum (diameter x heigh= 60 cm x 120 cm),

distillation pipe (diameter x heigh= 10 cm x 500 cm), cooler pipe (diameter x heigh= 10 cm x 200 cm). Distillation was used to purify the ethanol resulted from fermentation tank (6-12%) into 90-95%. Distillation operation was done by putting 150 liter fermented liquid containing ethanol 6-12% (v/v) into semi-automatic distillation system. Then, the liquid was heated until vapor was released toward distillate and cooler. During distillation process, cooler water was always flowed into cooler to keep the temperature at 79^{o}C.

2.5. Dehydration by means of adsorption

Adsorption unit consisted of stainless evaporator tank (40 cm x 60 cm), adsorption column containing adsorbent zeolite 3A (diameter x heigh= 30 cm x 100 cm), cooler column (diameter x heigh= 20 cm x 100 cm). The bioethanol resulted from distillation unit with the concentration of 90-95% was flowed to the evaporatio tank. The resulted vapor was then flowed through adsorption column.

2.6. Dehydration with membrane pervaporation

Membrane pervaporationunit consisted of stainless steel evaporator tank (diameter x heigh= 50 cm x 75 cm), membrane pervaporationmodule (diameter x heigh= 20 cm x 120 cm), vacuumpump and cooler column. Ten L of bioethanol were fed into evaporator column and then heatedup to a certain temperature. Thereafter, the bioethanol was pumped to the membrane module. The pressure in permeate side was adjusted at 6 mbars. After the operating condition was achieved, the process was operated for 2 hours. Permeate and retentate products were accumulated, weighed, and then analyzed.

2.7. Analysis ofreducing sugar and fermented ethanol

The concentration of reducing sugar was analyzed using oxidation reduction method using 3,5-dinitrosalicylic acid (DNS) followed by measuring its UV spectrum at 546 nm using UV/VIS spectrophotometer.The ethanol concentration was analyzed using GC-Hewlett Packard Agilent 6890N equipped with FID detector (flame ionization detector).

3. Results and Discussion

Ilesiles tuber analysis showed that the content of reducing sugar and starch were ~2% and ~79%, respectively. Detailed analysis of the basic material can be found in the previous publication [9]. Fig. 2 shows the result of GC analysis. Considering the result of GC analysis, the ethanol concentration obtained from fermentation of *Iles-iles* tuber is 8.8% (v/v).

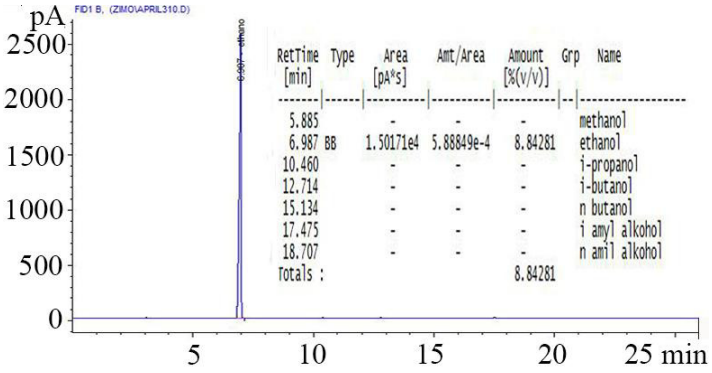

Fig 2.Result of analysis of ethanol from fermentation using GC

The effect of weight and fermentation time on reducing sugar and ethanol product is presented in Fig. 3. The

longer fermentation time, the higher ethanol level and the lower reducing sugar level are obtained. It suggests that the sugar content resulting from *Iles-iles* tuber saccharification can be converted into ethanol. Ruize et al. [10] reported that too high content of starch leads to decrease in conversion of starch into sugar in saccharification, which eventually lowers the fermented ethanol product. It is because too high content of starch hinders the diffusion of enzyme due to too thick starch. In this work the best the starch-to-water ratio is 1:3 and the yeast weight is fair.

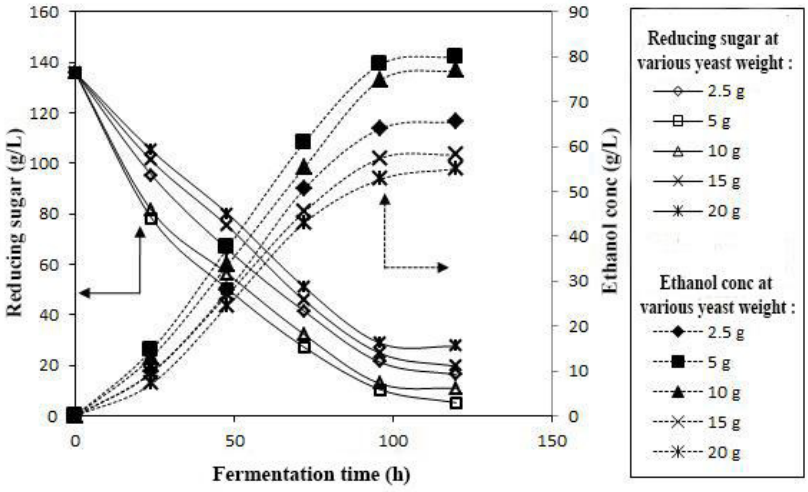

Fig 3.The effect of fermentation time on ethanol and reduced-sugar level.

It can be seen from Fig. 4 that the highest ethanol level was obtained in S. *cerevisiae* yeast weight of 5 g. Further increase in S. *cerevisiae*decreases the ethanol product. Oclo and Ayernor[11] stated that the yeast weight affects the fermentation rate but does not affect on ethanol quantity. After fermentation process, the ethanol 7-10% resulted from fermentation process was purified with distillation method. The comparison of distillation result using traditional unit and semi-automatic distillation can be seen in Table 1. It is found that the semi-automatic distillation unitworked faster than the traditional one to achieve the same ethanol concentration. To increase ethanol concentration from 70 to 90%, it is required 11 and 5.5 hours for traditional and semi-automatic distillation, respectively.

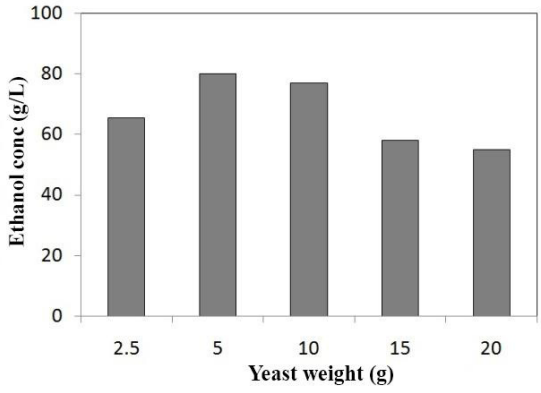

Fig 4.The effect of yeast weight on ethanol product, fermentation time = 72 hours.

Table 1.Result of distillation with traditional distillation unit and semi-automatic distillation unit

Ethanol vol. before distillation (% level)	Conventional distillation			Semi-automatic distillation		
	Time (hour)	Distillate vol. (liter)	Distillate level (%)	Time (hour)	Distillate vol. (liter)	Distillate level (%)
200 liter (10-12%)	3	40	35	-	-	35
120 liter (35%)	7	55	70	4	40	70
110 liter (70%)	11	90	90	5.5	60.5	90

Fig. 5 shows the experimental results of adsorption process for various concentrations of ethanol feed. It can be seen that the breakthrough time for ethanol concentration of 90% (v/v) appears in shorter time (60 minutes), while for feed of 95% in 120 minutes. It is because when the concentration of ethanol is low, the adsorption process proceeds in high partial pressure of water due to the larger volume of water. This result is in agreement with previous study by Pruksathorn and Vitidsant [7].

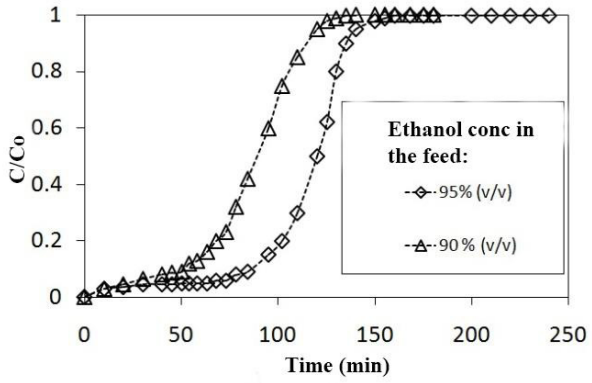

Fig 5.Adsorption process breakthrough curve in ethanol feed concentration variation with 90% and 95% (v/v).

To further increase of ethanol concentration membrane pervaporation was applied after adprtion process. The effects of feed concentration and operation time on the resulted ethanol are presented in Fig. 6. It can be seen that the ethanol flux increases as ethanol feed concentration was increased. This result is in line with the study of Al-Mayah et al. [12]. It is because the decreasing water flux is related to the equilibrium between water molecule and ethanol. In low ethanol concentration, water molecule is more than ethanol; therefore the water molecule dominates the diffusion through the membrane.The ethanol selectivity decreases as ethanol concentration increases in the feed. decreasing ethanol concentration leads to increase in water adsorption on membrane surface leading to more water in permeate side.

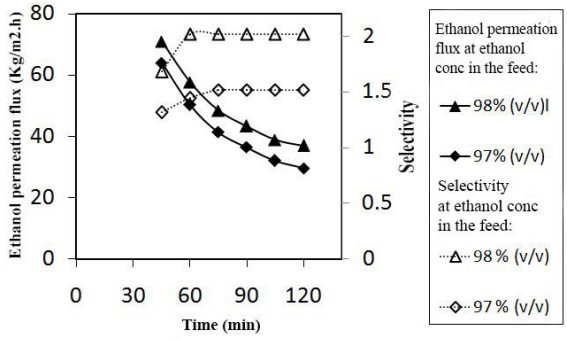

Fig 6.The effect of time and feed concentration on permeate ethanol flux and selectivity in membrane pervaporationprocess.

The effect of feed ethanol temperature (353 and 358 K) on ethanol flux and selectivity is presented in Fig. 7. The higher ethanol flux appears at 358 K compared with the one at 353K. The similar condition is seen in selectivity in which the selectivity increases as the temperature was increased. The effect of temperature has been studied by Zhan et al. [13] using composite membrane for ethanol dehydration, finding that the increase in temperature is proportional to the total flux. The effect of time on flux indicates that the steady state condition is achieved after 2-hour pervaporation process. The result of previous study using PERVAP 4060 membrane showed that steady state time was achieved after 4 hours [13].

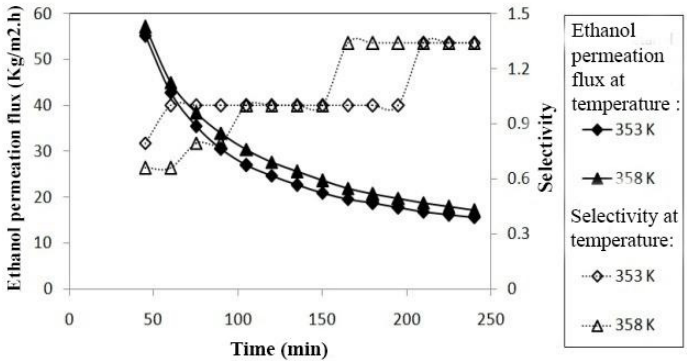

Fig 7.The effect of feed time and temperature on permeate ethanol flux and selectivity in membrane pervaporation process.

4. Conclusions

Iles-iles tuber can be used as basic material for bioethanol production. Hydrolysis reaction suggest that the best condition for Iles-ileshydrolysis is obtained at*Iles-iles*tuber-to-water ratio = 1:3, then heated at 90^{o}C for liquefaction process with α-amylase enzyme. Saccharification process with glucoamylase enzyme at 60^{o}C temperature produces simple glucose. In fermentation process for 72 hours, ethanol 50-80 g/L is produced for the concentration of S. *cerevisiae* yeast ranging between 2.5 to 20 g/L. The result of GC analysis shows ethanol peak in 6.5 minutes and ethanol level between 7-9% (v/v). Automatic distillation process yields ethanol 90% for5.5 hours operation. Adsorption process produces bioethanol 99%. The process with membrane pervaporation yields bioethanol concentration higher than 99% with steady state time achieved in 2 hours.

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