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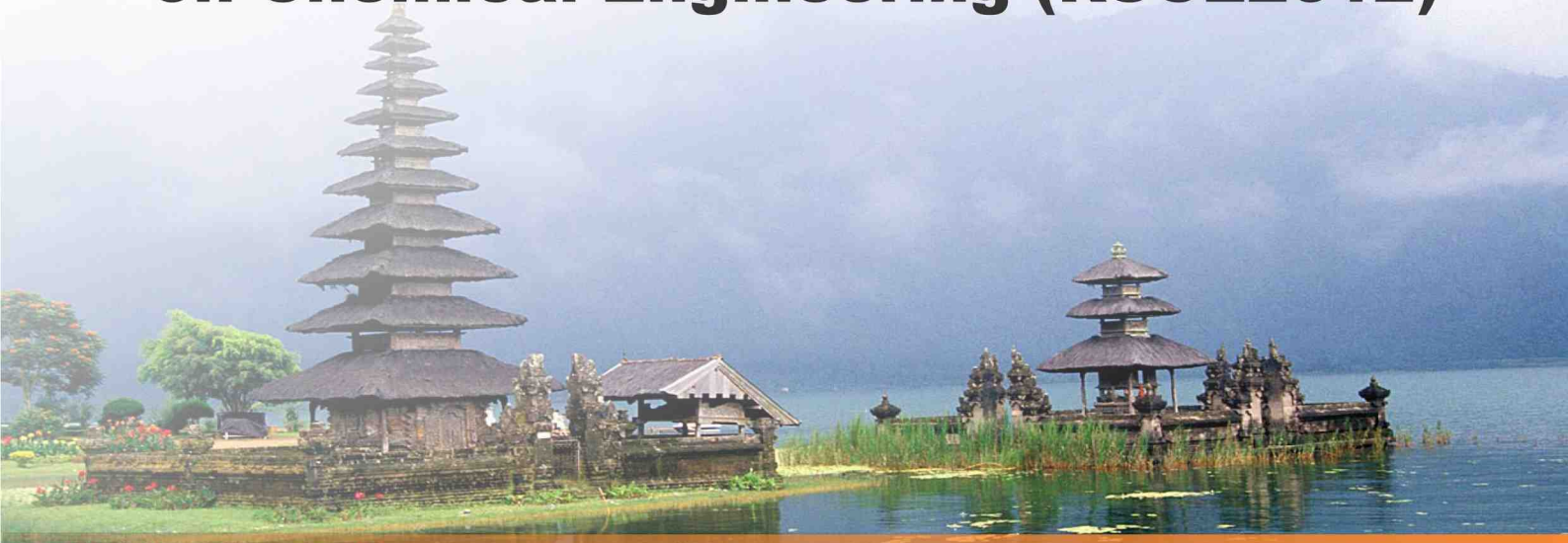

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Study of Bioethanol Production from Liquid Waste of Bogasari Factory in Mini Plant Scale

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Abstract

The availability of liquid waste from Bogasari factory can be maintained continuously and also available in huge volume. It is one of the liquid waste which is less attention. Besides, it contains a starch (carbohydrate) that can be used as an ingredient of ethanol. This research has a special purpose which is produce an bioethanol and a prototype of bioethanol industry. The future purpose of this research is this research can be used as an example in develop a bioethanol industry in Indonesia.

Refers to earlier research, rice contain for about 79% of starch and liquid waste from Bogasari factory contain 30% of starch. This value shows that liquid waste from Bogasari factory contains much starch. Production proses of bioethanol includes hydrolysis process of liquid waste from Bogasari factory with Bacillus, then it is continued with fermentation process of 'reduction sugar' (the result of hydrolysis of starch) with *Saccharomyces Cerevisiae* and ended by the distilation process in miniplant scale (100 litre ethanol/day in 3 batch). The quality is influenced by starch, glucose, pH, the ratio of waste (volume) and *Bacillus* (volume),*Saccharomyces Cerevisiae*, the length of fermentation and temperature of batch distilation.

This research is done in two years. The first year of research is for batch process to maintain the best condition which can be used for the main design of prototipe. The second year is for the continous process in testing and produce the prototipe process and produce the equipment for bioethanol production.

Keywords: Batch distillation, Fermentation**,** Hidrolysis, liquid waste of Bogasari factory.

1. Introduction

During this time, liquid waste of rice flour which is gained from PT Boga Sari's rice flour production process is not used well. That waste is processed as processing water only and discarded as a waste. Considering its nutrient and starch content, the liquid waste of rice flour factory has a potential to be processed further. One of the processing alternatives is to be made as an ethanol. Ethanol can be made from fermentation process by using *khamir* which is gained from liquid waste of rice flour factory. This process is started by hydrolysis process. The time to do this process depends on the kind of *khamir* that is used, initial glucose content and ethanol content that is required.

Based on lately research, the content of starch that can be gained from rice is about 79% while from liquid waste of PT Boga Sari, rice flour factory, can be gained about 30%. Production process of bioethanol involves hydrolysis process of liquid waste from Boga Sari Factory by using *Bacillus*, then continue by fermentation process of reduction sugar by using *Saccharomyces Cerevisiae* and distillation process in mini scale *plant* by scaling 100 liter ethanol/day in 3 batches. The quality of ethanol is influenced by starch and glucose content, acidity degree (pH), ratio between waste and *Bacillus* volume, the amount of *Saccharomyces Cerevisiae* bacteria, time of fermentation process and temperature of distillation batch.

In expanding the high production of ethanol, needing the study about the requiring ingredients, reaction mechanism, and technology. The most influenced factor here is ingredients, hydrolysis process, fermentation process and batch distillation process.

2. Theory (or Experimental)

Liquid waste from Boga Sari Factory is a form of *leri* water, water that is gained from washing process of rice that is used to make flour. The content of *leri* water (2 kg rice : 1 liter water) as

shown in Tabel 1. In tabel 1 can be seen that *leri* water consists of organic compound such as carbohydrate and thyamin which is a nutrient compound that still can be used for khamir's growth that is usefull in production process of ethanol (Munadjim, 1990).

Table 1. Nutrient Content of *Leri* Water

Composition	Amount (mg/lt)
Fat	90,0
Protein	420,0
Carbohydrate	300,0
Calsium	20,0
Phosphor	200,0
Iron	1,8
Vitamin B	0,9

Source : Badan Penelitian dan Pengembangan Industri (1990)

Carbohydrate is the main source of calori for human beside protein and fat. Empirical formula of carbohydrate is $(CH_2O)_n$. Carbohydrate has a main role to determine the charateristic of food such as taste, colour, texture, and etc. While in the body, carbohydrate is usefull to prevent the occuring of an exaggerate protein breaking, losing of some minerals, and to help fat and protein metabolism. In the nature, carbohydrate is formed from the reaction between CO_2 and H_2O with the sunlight by photosynthesis process in some plants which have chlorofil. Carbohydrate can be found from the root and stem such as sago. The sources of carbohydrate that are the main food in many areas of Indonesia is in a form of seed such as rice and corn.

In general, carbohydrate can be categorized in three part, there are:

a. Monosaccharide

Monosaccharide is a molecule that consists of 5 or 6 C atoms. Monosaccharide that has one aldehide group is aldosa. While ketosa has one group of keton. Monosaccharide with 6 C atoms is hexosa, such as glucose (dekstrosa/ wine sugar). While monosaccharide which has 5 C atoms is pentosa such as xilosa, arabinosa and ribose.

b. Oligosaccharide

Oligosaccharide is a polymer from 2-10 monosaccharide. Usually, it is soluble in water. Oligosaccharide which consists of 2 molecules of monosaccharide is disaccharide. The example of disaccharide is sukrose. Oligosaccharide can be gained from polysaccharide hydrolysis by using certain enzyme or hydrolysis by acid.

c. Polysaccharide

Polysaccharide is complied by many molecules of monosaccharide. Polysaccharide in food has a function as texture amplifier (selulose, hemiselulose, pectin, and lignin) and as a source of energy (starch, glicogen, and fructan) (Winarno, 1984).

Glucose is the most monosaccaride in the nature as a product from photosynthesis process. In the free form, it is found in some fruits, some plants, honey and blood. In the bonding form, it can be found in animal's body as glicosida and in plant as disaccharide ang polysaccharide. Glucose can be gained from polysaccharide and disaccharide by using acid or enzyme. As aldohexosa, glucose has 6 C atoms in its molecule chain. One end of that is an aldehide group. Carbon atoms number 2 until 5 in the chain is chiral group. So, there are 16 posibility of isomer configuration in glucose. From all isomer configurations, a half have been identified in the nature, and the remain must be made synthetically. Not less than 32 kinds of organism have been observed that can produce glucose isomerase such as *Pseudomonas, Aerobacter, Escherchia, Bacillus, Brevibacterium, Paralactobacterium, Leuconostoc*, dan *Streptomyces* (Soebijanto, 1986).

The result from glucose fermentation is ethanol which ethanol has a basic formula C_2H_5OH and has physical properties such as : colourless liquid, typical smell, volatile, boiling point is 78.32 ^oC, soluble in water and ether, density in 15 ^oC is 0.7937 ; heat specific in 20 ^oC is 0.579 cal/gr ^oC, heat of combustion in liquid condition is 328 Kcal, viscocity in 20 ^oC is 1,17 cp, flash point is about 70 ^oC. Chemical properties of ethanol : molecule weight is 46.07 gr/mole, occuring from monosaccharide fermentation reaction, react with acetic acid, sulfate acid, nitric acid, ionida acid (Soebijanto, 1986).

Ethanol requirement in the world is increasing. It can be seen in national ethanol requirement as following :

Table 2. The amount of national ethanol requirement

Year	Ethanol requirement (liter)
2001	25.251.852
2002	21.076.317
2003	34.063.193
2004	230.613.100
2010	2.939.456.115

Source: Badan Pusat Statistik, Surabaya (2010)

In trading world, known a quality level of ethanol as following :

a. Technical alcohol (96,5 ºGL). It is used mainly for industrial needs. As organic solvent, fuel, and also for raw materials or another organic compound production.
b. Rubbing alcohol (88 ºGL). This substance is usually used as a fuel for room heating and lighting tools.
c. Absolute alcohol (99,7 - 99,8 ºGL). It is most used in many production process of medicine and also solvent materials or as a material to make another compounds in laboratory scale.
d. Pure alcohol (96,0 - 96,5 ºGL). This kind of alcohol is mainly used for pharmacy and consumption needs (liquor and etc) (Soebijanto, 1986).

Some substances that contain monosaccharide ($C_6H_{12}O_6$) such glucose can be directly processed to be an ethanol. However starch disaccharide, complex carbohydrate must be hydrolysed first to be simple component such monosaccharide. Fermentation process can be held optimally, that substances must be given a preliminary treatment before going to the fermentation process. Disaccharide such granulated sugar ($C_{12}H_{22}O_{11}$) must be hydrolysed to be a glucose, polysaccharide such selulose must be changed first to be glucose. The forming of glucose means that the preliminary process has been done and the next substances are ready to be fermentated. Chemically, fermentation process can be held quite long, because there are a reaction row which each reaction is influenced by special enzymes.

HYDROLYSIS

Starch is a more complex component than disaccharide, before the fermentation process is started, starch must be disparted by using amylase enzyme (most in germinated wheat) to be a disaccharide component such maltose. By using another enzyme, maltase, maltose can be hydrolysed to be glucose (Gumbira, 1987).

$$(C_6H_{10}O_5)_n + 1/2n\ H_2O \xrightarrow{\text{Amylase enzyme}} 1/2n\ C_{12}H_{22}O_{11}$$

$$1/2n\ C_{12}H_{22}O_{11} + 1/2n\ H_2O \xrightarrow{\text{Maltase enzyme}} 1/2n\ C_6H_{12}O_6$$

Hydrolysis process is influenced by some factors such as the carbohydrate content in raw materials, pH operation or the using acid concentration, time of hydrolysis, hydrolysis temperature and catalyst.

FERMENTATION

Ethanol is a natural form that is produced from fermentation process that is most found in beer product, wine, rubbing alcohol and many more. Alcoholic drinking can be categorized into two parts, that are : Fermentation product which is consumed directly and fermentation product which must be distillated first before consumed.

In the forming of alcohol through fermentation process, the role of microbiology is important and usually microbiology which is used for fermentation has some requirement as following :

Having a ability to do matched carbohydrate fermentation promptly, can form frakulasi and sedimentation, having a stable genetic (not prone to mutation), tolerant of high alcohol (about 14 – 15 %), having a rapid regeneration (Kartika, 1992).

Alcoholic drinking that is produced without distillation (fermentation product) usually has a content of alcohol between 3 – 18 %. To increase the content of alcohol in the product, frequently fermentation product is distillated and alcohol content that is produced between 29 – 50 %. The principle, the reaction process of forming ethanol by fermentation as following :

$$C_6H_{12}O_6 \xrightarrow{Khamir} 2\,C_2H_5OH + 2CO_2$$

In the yield of fermentation usually formed a dilute alcohol liquid, because *khamir*'s cells will be died if the content of ethanol more than 12 – 15 % (Gumbira Sa'id, 1987). An ideal fermentation yield is 51,1 % ethanol and 48,9 % carbon dioxide. The optimum alcohol fermentation yield is indicated in % fermentated glucose, such: Ethyl alcohol 48,8 %, carbon dioxide 46,6 %, Glycerol is 3,3 %, succinate acid is 0,6 %, selulose and the remain is 1,2% (Soebijanto, 1986).

Factors that affect in fermentation process are the good pH for fermentation between 4-5, because lactate acid is good for yeast growth, but the negative effect is butyrate acid bacteria can grow which can be harm for yeast fermentation (Bahri, 1987). The time that is needed for fermentation depends on temperature, consentration of sugar and generally the requiring time is between 36 – 50 hours (Bahri, 1987). In general, the good temperature for fermentation process is between 25 – 30 ºC. The lower temperature of fermentation, the higher alcohol content that is produced. This condition happens because in the low fermentation temperature will be more complete and lose alcohol because is brought by less carbondioxide (Agus, 2002).

The speed of fermentation is influenced by salt consentration, activity and growth of *khamir*, while the high consentration will obstruct the khamir's growth. The elements that are needed for khamir's activity are Mg, K, Zn, CO, Fe, Ca, Cu, P, S, and N. As the source of P and N, ammonium phospate needs to be added. As the other source of N, ammonium chloride and ammonium carbonate can be added. Vitamin has a function as a khamir's growth factor (Agus, 2002). Sugar that is added has a purpose to get a higher alcohol content, although sugar content is too high, khamir's activity can be obstructed. The good sugar content for preliminary fermentation is 16 %. This is for accelerating khamir's growth in preliminary fermentation. The optimum sugar content for khamir's growth activity is 10 % (Agus, 2002).

DISTILLATION BATCH

Differential distillation is usually done in batch way by using distillation vessel. The yield steam (Vm) is immediately condensed and distillated (D) are separated from the remaining liquid in vessel (W). Because the steam consists of more volatile substance so residual content which is more volatile will be decreasing. In the separating multicomponent system, it is assumed that liquid perfectly mix which $x_w = x_i$ and $y_D = y_i$, so (*Henley* dan *Seader*, 1998). Where liquid composition in *bottom* (x_w), liquid component composition i (x_i), steam composition in distilat (y_D) and steam component composition i (y_i). Defined *dimensionless* time (ξ) is as following: Where, ξ = dimensionless number which depends on time, substituted so obtaininge equation :

$$\frac{dx_i}{(y_i - x_i)} = d\xi \qquad (1)$$

Equation above is *Differential-Algebraic-Equations* (DAEs) model for multi component simple distillation batch, with the asumption doesnot produce two liquid phases. Equation above with *forward-finite-difference*, will be obtained liquid composition in *bottom* ($x_{i,j+1}$) as function $\Delta\xi$, so it can be obtained as following:

$$x_{i,j+1} = x_{i,j} + (y_{i,j} - x_{i,j})\,\Delta\xi \qquad (2)$$

Which initial liquid composition in *bottom* ($x_{i,j}$) and $\Delta\xi$are determined, while steam composition ($y_{i,j}$) is counted by using BUBL T equation (*Henley* dan *Seader*, 1998).

3. Results and Discussion

According to the result of laboratory analysis, the amount of bioethanol forming elements (glucose and starch), the average number of starch is for about 9.282 %. If all of that is hydrolysed perfectly, it will be gained high glucose content. In 100 liter liquid waste of Boga Sari, rice flour factory,it will produce maximum glucose content for 9.282 liter. Beside starch, there is also a high glucose content in liquid waste of Boga Sari Factory. In 100 gram liquid waste of Boga Sari Factory, it will produce maximum glucose content for 3.786 liter. Due to the high content of glucose and starch in liquid waste of Boga Sari Factory, the hydrolysis process is expected to be done perfectly. So the content of glucose and starch content will be degradated perfectly to become 12.568 liter of glucose.

The filtering process of liquid waste from Boga Sari Factory is held by using gauze. The filtering process is done repeatedly to gain a pure result before doing a hydrolysis process. The sedimentation process will be done naturally by stopping that process in a few time. Then the filtrate is taken and the sediment is used as compost. Before doing hydrolysis process, filtrate's pH is measured based on the fermentation process requirement for about 4.5. To maintain the pH stable in 4.5, the addition of NaOH is done when the filtrate's pH is under and the addition of citrate acid is done when the filtrate's pH is above 4.5 (Sari, 2009).

Hydrolysis process is held by *Bacillus*'s ratio of varies waste volume, that is 1:2 ; 5:4 ; 10:7 with adding a varies *Bacillus* volume : 5, 7, 9, 11, 13 (%v/v). After finishing hydrolysis process, it will produce filtrate and solid form. Filtrate will be processed by fermentation to gain ethanol content while the solid form can be used as compost. Before holding a fermentation process, the maximum glucose content of filtrate is measured less than 16 %. If the glucose content is more than 16 %, the dilution process must be done. If the glucose content is less than 16 %, water evaporation of materials must be done (Sari, 2007).

The affect of glucose content to the *Bacillus* volume addition is the higher *Bacillus* volume addition, the higher glucose content will be. In addition of *Bacillus* volume above 9 %v/v, the graph shows the constant profile, because the activity of *Bacillus* is decreasing and will be died slowly then needs the regeneration of *Bacillus*. The addition of *Bacillus* volume between (3-9) %v/v shows that the glucose content is increasing, because of the growth phase of *Bacillus* which decomposes starch to be glucose maximally.

The fermentation process of rice flour factory's liquid waste filtrate from Bacilus ratio of a varies waste volume, that is : 1:2 ; 5:4 ; 10:7 by adding a varies *Saccaromycess Sereviceai* : 5, 7, 9, 11, 13 (%v/v) with time of fermentation 4, 6, 8, 10, 12 days. For fermentation process, it is used Bacillus ratio variabel of liquid waste volume that is 1:2 ; 5:4 ; 10:7. Every *Bacillus* ratio of liquid waste volume each is wanted glucose and the remain starch content. After holding anlysis of the remain glucose content in fermentation process, with adding the amount of sacharomyces 7 %v/v from liquid volume (filtrate), shows that the remain glucose content is lower than the addition of starter 6, 9, 11 and 13 %v/v. This is caused by the preliminary research and based on the Jurnal that is addition 7 %v/v from liquid volume (filtrate).

The affect of filtration rate to the remain glucose content for the amount of *saccaromyces cereviceae* starter 6, 9, 11 dan 13 %v/v, obtaining the maximum remaining glucose content of (1.5 – 5) % (Sari, 2006). This is caused by the low content of filtrate from hydrolysis process and *saccaromyces cereviceae* starter in reactor tank then the fermentaion process has not been done maximally. By the increasing of filtrate from hydrolysis process and *saccaromyces cereviceae* starter, the remain glucose content will be decreasing because it has been fermentated become ethanol.

The maximum ethanol content of fermentation process is 20.15 % and the minimum content of ethanol is 7.3 % while the yield of fermentation in general is 10-16 %. This is caused by the fermentation process which is done well. Beside that, it works optimally in starter addition of 7 %v/v. Ethanol content of filtration rate is 0.6 %. Ethanol content reaches the maximum number of 20.15 %, then it is decreasing slowly until the filtration rate reaches 1.0 %. This is happened because there is an adaptation process between *saccaromyces cereviceae* and the filtrate from hydrolysis process of rice flour factory's liquid waste in the initial fermentation process. After the

saccaromyces cereviceae starter reaches 7 %, there will be a maximum fermentation process with the increasing of the ethanol yield and good working of *saccaromyces cereviceae*. After that, the regeneration process of *saccaromyces cereviceae* will be done to regenerate the dying *saccaromyces cereviceae*. In the fermentation process, the allowing glucose content is between (14 - 16) % with pH (3 – 4.5), so it can be obtained ethanol content for about 20.15 %. Fermentation process has been done well and reaches the maximum yield.

4. Conclusion

Based on the research result, the best result of hydrolisis process can be reached in *Bacillus* ratio to the liquid waste of rice flour 10 : 7, 9%v/v *Bacillus*, glucose content 9.88 % of weight. In fermentation process, the best result can be reached in *saccharomyces cerevisiae* content of 7 %v/v, time of fermentation is 10 days, ethanol content is 20.88 % and remain glucose content 2.44 %. The quality of ethanol that will be gained after holding a distillation batch is 92-96 % and the yield reaches 33.3 %.

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