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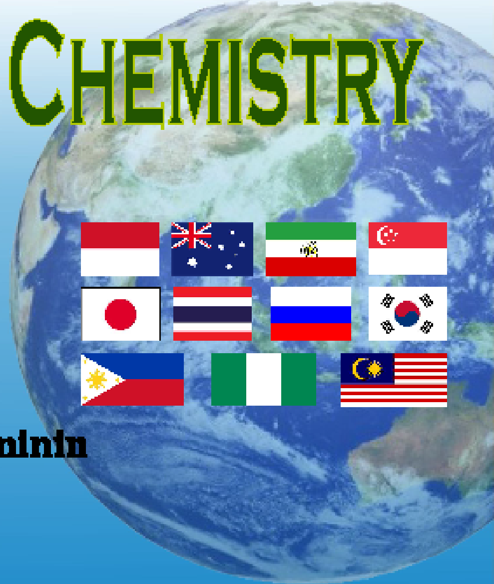

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Menyatakan bahwa makalah berjudul *"The Effects of Hydrolysis Temperature and Catalyst Concentration on Bio-ethanol Production .from Banana Weevil"* karya **Eni Budiyati dan Umar Bandi** dari Program Studi Teknik Kimia, Fakultas Teknik, Universitas Muhammadiyah Surakarta. Telah dipresentasikan pada ***9th Joint Conference on Chemistry 2014*** yang diselenggarakan oleh Universitas Diponegoro Semarang, Universitas Negeri Semarang, Universitas Negeri Sebelas Maret, dan Universitas Jenderal Sudirman Purwokerto pada tanggal 12 – 13 Nopember 2014 di Grand Candi Hotel Semarang.

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The Effects of Hydrolysis Temperature and Catalyst Concentration on Bio-ethanol Production from Banana Weevil

Eni Budiyati[a] and Umar Bandi[a]

Abstract

An energy need of petroleum fuels in various countries in the world in recent years has increased sharply. It doesn't only happen in the developed countries but also in developing countries, including Indonesia. Scientists have a develop a renewable energy source to anticipate the crisis of petroleum fuels. Several types of renewable energy are biomass, geothermal, solar energy, water energy, wind energy, and ocean energy. Ethanol is a bio-fuel, and has good prospects as a substitute for liquid fuel and gasohol with renewable raw materials and environmentally friendly. Four steps are applied in this study. The first is preparation of tools and raw materials. All instruments were sterilized and banana weevil as raw material is cut and grind. The second is hydrolysis process, which HCl is used as catalyst. in the process,temperature are varied at 70 °C, 80 °C, 90 °C, and concentration of catalyst are 0.1; 0.2; and 0.3 N. The third step is fermentation, which is conducted at the ambient temperature (27 °C) and anaerobic conditions. The last is distillation process. The results show the greater hydrolysis temperature, the concentration and the yield of produced bio-ethanol greater. The hydrolysis process of HCl 0.3 N at 90 °C, resulted in the greatest level of bio-ethanol, which is 61.20%. This research should be developed, especially for the purification process on order to obtain higher ethanol concentration.

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Introduction

Ethanol is a bio-fuel, has good prospects as a substitute for liquid fuel and gasohol with renewable raw materials, environmentally friendly and very beneficial economically for rural communities, especially farmers. According to the Energy Minister's decision No. 32 of 2008 "bio-ethanol (E100) is product of ethanol produced from biological raw materials and other processed biomass in biotechnology and shall meet the quality standard (specification) in accordance with the provisions of the legislation to be used as alternative fuel ".

This study used banana weevil as raw material for bio-ethanol production because the banana weevil has a composition of 76% starch, 20% water, and the rest is protein and vitamins (Yuanita et al., 2008). The benefit to the community is this process can reduce banana plant waste, especially banana weevil. Besides that, it can be used to raise the added value of banana weevil into valuable chemical. Industry of ethanol in Indonesia can use banana weevil as an alternative to the manufacture bio-ethanol, as a reference and development potential hump banana biomass as a feedstock for bio-ethanol production.

Banana (*Musa paradisiacal*)

Banana (*Musa paradisiacal*) is an herbaceous fruit plants originating from areas in Southeast Asia. These plants then spread to Africa (Madagascar), South and Central America. Bananas in West Java called "cau", in Central Java and East Java called "gedang". Banana plants can be easily found almost in every place. Banana production centre in West Java is Cianjur, Sukabumi and the area around Cirebon. Bananas are generally able to grow in the lowlands to the mountains with an altitude of 2000 m. Bananas can grow on wet tropical climate, humid and hot with optimum rainfall is 1520-3800 mm/year with 2 months to dry (Rismunandar, 1990**)**.

Banana weevil can be used to be taken the starch, this starch resembling sago starch flour and tapioca flour. The potential content of banana weevil starch can be used as an alternative fuel that is, bio-ethanol. Starchy materials are used as raw material for bio-ethanol suggested that high levels of starch, has a high yield potential, flexible in farming and harvesting (Prihandana, 2007 and Aswandi et al., 2012).

Table 1. Chemical content of 100 gram banana weevil

No	Component	Wet	Dry
1	Starch (gram)	96	76
2	Calories (cal)	43	425
3	Protein (gram)	0.6	3.4
4	Carbohydrates (gram)	11.6	66.2
5	Ca (mg)	15	60
6	P (mg)	60	150
7	Fe (mg)	1	2
8	Vitamin C (mg)	12	4

Bio-ethanol

Bio-ethanol production is determined by: 1) number of raw material, 2) the amount of sugar that ready to be fermented, and 3) efficiency of fermentation process to convert sugar into alcohol (Smith, et al., 2006). Bio-ethanol is ethanol (ethyl alcohol) produced using natural raw materials and biological processes. Ethanol is used as a vehicle fuel has a chemical structure that is identical to that found in ethanol liquor. Ethanol used for fuel called by Fuel Grade Ethanol (FGE) with a purity level of 99.5%. Ethanol is an organic compound composed of carbon, hydrogen and oxygen. So it can be viewed as derivatives of hydrocarbon compounds having a hydroxyl group with the formula C_2H_5OH (Hendroko, 2008).

Characteristics of ethanol:

a. Physical properties of ethanol

Molecular weight	: 46.07 g/mol
Colour	: No Colour
Phase	: Liquid
The normal boiling point	: 78.4 °C
Freezing Point	: -112 °C
Specific Gravity	: 0.7893
Solubility in 100 parts Water	: Infinity
Other reagents	:Infinity (Perry, 2007)

b. Chemical properties of ethanol

Burning ethanol produces carbon dioxide and water:

$$C_2H_5OH\ (g) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O\ (l)$$

Ethanol can be used as an automotive fuel is varied, from blend to pure bio-ethanol. Bio-ethanol is often referred to by the notation "Ex", where x is the percentage of ethanol content in the fuel. Some examples of the use of the notation "Ex" are:

1. E100, 100% bio-ethanol or without a mixture
2. E85, a blend of 85% bio-ethanol and 15% petrol
3. E5, a mixture of 5% bio-ethanol and 95% petrol

PERTAMINA has sold bio-premium (E5) containing 5% bio-ethanol and 95% premium. E5 fuel can be used on vehicles that use petrol (gasoline) standard, without any modification. However, E15 fuel up or a percentage of more than 15% ethanol must utilize the vehicle with the type of Flexible-Fuel Vehicle. Brazil as one of the countries that use the world's largest bio-ethanol, has adopted the E100 fuel, which contains 100% bio-ethanol (Atmojo, 2010).

Hydrolysis

Hydrolysis is a process of the reactants with water to break compound. in the hydrolysis of starch with water, the water will attack the starch on α 1-4 glucosidal bond form dextrin, syrup or glucose depending on the degree of starch breakdown in the polysaccharide chain. Reaction is first order reaction if excess water is used, so that changes of reactants can be ignored. The reaction between water and starch goes so slowly, so it needs a catalyst to increase the reactivity of water. This catalyst can be acidic, alkaline or enzyme (Coney, 1979 in Retno 2009).

Hydrolysis process of starch into sugars is required following reaction:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow n(C_6H_{12}O_6)$$

Polysaccharides Water Glucose

The Influence variables of the hydrolysis reaction:

a. Catalyst

Almost all of the hydrolysis reaction requires a catalyst to accelerate the reaction. The catalyst used can be either enzymes or acid. The acids usually used are hydrochloric acid (Agra et al., 1973; Stout & Rydberg Jr., 1939 in Prasetyo, 2011), sulphuric acid, and nitric acid. The H ion concentration give bigger affect to reaction rate than the type of acid. Nevertheless, generally the industry use hydrochloric acid. This selection was based on the salt formed in neutralization reaction. Sodium chloride is safe and there is dangerous when the concentration is too high (just give salty taste). So, the acid concentration in water is controlled. Commonly acid solution concentration that used has a higher than concentration of acid in the manufacture of syrup. Hydrolysis at a pressure of 1 atm requires a much more concentrated acid. The rate of hydrolysis process will increase by a high concentration of acid. in addition to adding the rate of hydrolysis process, a high concentration of acid will also result in binding of ions such as SiO_2 controller, phosphate, and salts such as Ca, Mg, and Na in starch. Therefore, the appropriate comparison is required between the starch will be hydrolysed to the acid concentration (Sun and Cheng, 2005).

b. Temperature and pressure

The influence of temperature on the reaction rate follows Arrhenius equations. The higher temperature will increase the reaction rate. for example, to achieve a certain conversion takes about 3 hours to hydrolyse starch sweet potatoes at 100 °C. But if the temperature is raised to a temperature of 135 °C, the reach the same conversion can be reached in 40 minutes (Agra et al., 1973 in Prasetyo, 2011). Wheat and corn starch hydrolysis with sulphuric acid catalyst requires a temperature of 160 °C. Since the heat of reaction is almost close to zero and the reaction in the liquid phase, the temperature and pressure are not much affect the balance.

c. Mixing (stirring)

Reaction rate will be faster if reactants can collide with each other as well as possible, so mixing is needed. for a batch process, this can be achieved by use stirrer or shaker (Agra et al., 1973 in Prasetyo, 2011). If the process is a process flow (continuous), then the mixing is done by regulating the flow in the reactor in order to increase turbulence.

d. Comparison of reagents

If one of the reactants is excessive amount then the balance may shift to the right as well. Therefore, low levels of starch suspension may give better results than high starch levels. If levels of suspense lowered from 40% to 20% or 1%, then the conversion will increase from 80% to 87 or 99% (Groggins, 1958). At the surface level, high starch suspense molecules will be difficult to move.

The five types of hydrolysis, namely:

a. Hydrolysis in Acid Solution

Dilute or concentrated acid such as HCl, H_2SO_4 (other expensive acid) are usually serves as a catalyst. in dilute acid, commonly, the reaction rate is proportional to the concentration of H or $[H^+]$. These properties do not apply to concentrated acid. High sugar efficiency recovery as well as the potential for cost reduction, is most significantly the advantage of the acid hydrolysis process (Matz, 1970 in Retno, 2009).

The weakness of the acid hydrolysis is degradation of sugars results in the hydrolysis reaction and the formation of undesired products. Degradation of sugar and side product will not only reduce the sugar harvest, but side product also can inhibit the formation of ethanol in the next fermentation stage.

b. Bases in the hydrolysis solution

Dilute or concentrated bases used in the hydrolysis reaction are NaOH and KOH. Result of this process is not acid but salt. Two main advantages of this method are the reaction is occur irreversible and its products more easily to be separated. However, a potential problem regarding the disposal of waste is the disadvantage of this process.

c. Hydrolysis with enzyme as catalyst (Retno et al, 2011)

An α-amylase is one of enzymes produced by microbes. The advantage of enzymatic hydrolysis is able to degrade complex carbohydrates into simple sugars with more results. However, enzymatic hydrolysis also has some weaknesses such as low hydrolysis rate and expensive cost.

d. Pure hydrolysis

Reacted with H_2O without catalyst, the reaction is slow so rarely used in the industry. This process is suitable for reactive compounds. The reaction can be accelerated by using H_2Ovapour.

e. Alkali Fusion

Either with or without H_2O at high temperatures, e.g. in solid NaOH (H_2O<<). Usage in the industry for a specific purpose, such as smelting cellulosic materials such as corn cobs, "grajen" wood performed at high temperature (± 240 °C) with solid NaOH produces oxalic acid and acetic acid.

Fermentation

Ethanol fermentation, referred to as alcoholic fermentation, is a biological process in which sugars such as glucose, fructose, and sucrose are converted into cellular energy and also produce ethanol and carbon dioxide as by-products. This process does not require oxygen, then the ethanol fermentation is classified as anaerobic respiration. Fermentation ethanol is used in the manufacture of alcoholic beverages, ethanol fuel, and added agent in bread cooking.

The types of fermentation are:

1. Alcoholic fermentation

Alcoholic fermentation is a conversion reaction of glucose to ethanol (ethyl alcohol) and carbon dioxide.

$$C_6H_{12}O \xrightarrow[\text{(yeast)}]{\textit{Saccharomyces cerevisiae}} 2CO_2 + 2C_2H_5OH$$

2. Lactic acid fermentation

Lactic acid fermentation is that respiration occurs in animals or human cells, when the oxygen requirement is not fulfilled due to overwork. in the muscle cells, lactic acid can cause symptoms of cramps and fatigue. Lactate accumulated as waste products can cause muscle fatigue and pain, but gently transported by the blood to the liver to be converted back to pyruvate.

3. Fermentation of vinegar

It is an example of fermentation that takes place in the aerobic condition. Fermentation is carried out by acetic acid bacteria (*Acetobacter aceti*) with the ethanol as substrate. The energy produced 5 times greater than the energy produced by anaerobic fermentation of alcohol

Influence factor of bio-ethanol fermentation are: media, temperature, nutrition, pH, volume starter, fermentation time, concentration of sugar (Azizah et al., 2012).

Distillation

Distillation is a method of separating the components of a mixture by using heat as the energy separation based on boiling point of each component. Distillation unit operation is a method used to separate the components of a liquid solution, which depends on the distribution of the various components between vapour and liquid phases. The basic requirement for the separation of components by distillation is the composition of the vapour will be different from the composition of the fluid that is in equilibrium at the boiling point of the liquid. Distillation associated with a solution in which all the components are volatile, such as in water-ammonia or ethanol-water solution, where both components will be in the vapour phase. in evaporation, a solution of salt and water, the water evaporates, but the salt is not. Different absorption process of distillation that one of the components in the absorption is essentially insoluble in the liquid phase (Geankoplis, 1993)

Methodology

This research is conducted at Laboratory of Chemical Engineering Department, Muhammadiyah University of Surakarta.

Tools and materials

Tools in the manufacture of bio-ethanol are: heating mantle, three-neck flask, thermometer, condenser, erlenmeyer, pipette, flask, measuring cup, beaker glass, glass funnel, filter paper, spray bottle, glass stirrer.

The materials used are: banana weevil, HCl, NaOH, urea, *Saccharomyces cerevisiae,* methylene blue indicator, Fehling A, Fehling B, distilled water.

Research procedure

This study use four steps, namely:

1. Preparation tools and raw materials

Sterilization of equipment. All instruments were sterilized by autoclaving at a pressure of 15 psi and temperature of 121 °C for 15 minutes, and then cooled.

Preparation of starch banana weevil
- ✓ Banana weevil is cut into small pieces.
- ✓ Enter banana weevil in the oven until dry.
- ✓ Grind small hump-shaped and banana until smooth.

2. Hydrolysis

Weighing 50 g starch banana weevil then added a solution of 0.1 N, 0.2 N and 0.3 N of 250 ml. Pouring the solution into the three-neck flask, installing a hydrolysis and heat with a temperature variation of 70 °C, 80 °C, 90 °C, and once reached, the temperature is maintained then every 45 minutes to take samples for analysis of glucose levels using the Lane-Eynon method. Wait the product of hydrolysis is cool (at room temperature), then hydrolysis product is filtered and neutralized by adding NaOH 0.1 N. Furthermore, the product of hydrolysis is analysed the glucose levels by using the Lane-Eynon method.

3. Fermentation

- ✓ Solution fermentation medium is inoculated with a starter into a sterilized Erlenmeyer.
- ✓ Sealed bottle fermentation and connected by plastic tubing inserted into the water.
- ✓ Analyse glucose fermentation solution, after 24 hours of fermentation is stopped.

4. The distillation process

The process of distillation is carried around 80 °C. Furthermore distilled alcohol was analysed to determine the ethanol concentration.

Results and Discussion

Hydrolysis carried out on the milled banana weevil. Temperature of hydrolysis process is varied at 70 °C, 80 °C, and 90 °C. Concentration of HCl as catalyst are 0.1 N, 0.2 N, and 0.3 N. Product of hydrolysis is entered into fermentation process during 3 days, then it is distilled at a distillation temperature of 80 °C for 3 hours.

Table 2 and Figure 1 show that the greater hydrolysis temperature, the greater levels of ethanol. It can be explained, the increasing of temperature will increase the reaction rate constant. Automatically, reaction will be faster and level of ethanol will rise. It is also suitable with the Arrhenius law. Besides that, they also give information that ethanol level increase by increasing concentration of HCl. in the hydrolysis process, H^+ from HCl will convert the starch of the banana weevil group into clusters of free radicals. Cluster of free radicals then binds to the OH^- group of water and reacted at a temperature of 90 °C for 2.5 hours which will produce glucose. At HCl concentration of 0.1 N, ethanol level reaches the optimum temperature at 80 °C. It is different with the data at the HCl concentration of 0.2 N and 0.3 N, ethanol level has not reached the optimum point. When the HCl concentration of HCl is 0.2 N, H^+ is insufficient. As a result, the free radical clusters formed from banana weevil is not optimum, so the resulting glucose is not maximized. Addition of HCl concentration will form more free radicals starch group, but the addition of HCl concentration causes the less water in the solution hydrolysis, which it can reduce the produced glucose. The highest ethanol level in this research was 61.20% (at 90 °C and 0.3 N HCl)

Table 2. Ethanol Level Data at Varied Temperature and HCl Concentration

Temperature (°C)	Concentration of HCl (N)	Ethanol level (%)
70	0.1	37.84
80	0.1	42.19
90	0.1	42.98
70	0.2	48.30
80	0.2	53.75
90	0.2	59.41
70	0.3	50.20
80	0.3	55.67
90	0.3	61.20

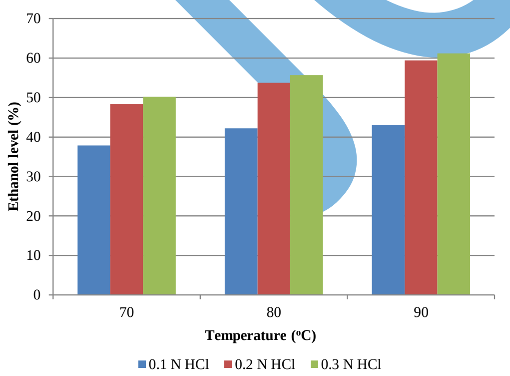

Figure 1. Ethanol Level at Varied hydrolysis Temperature and Concentration of HCl.

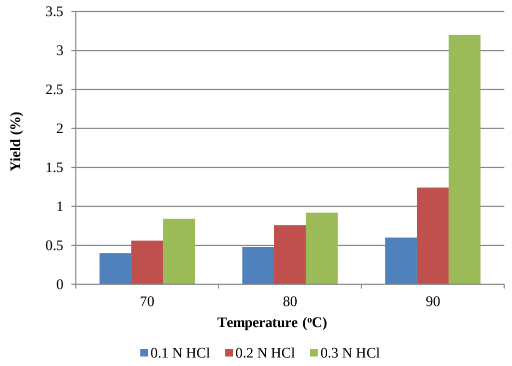

Figure 2. Ethanol Yield at Varied HCl Concentration and Hydrolysis Temperature

Figure 2 shows that the greater hydrolysis temperature, the greater of resulting yield. This is due to the high temperature causes the distance of carbohydrates particles will be longer; therefore it make the acid will easier to cut the carbohydrates chain into glucose. The highest of ethanol yield is occurred at a temperature of 90 °C and the HCl concentration of 0.3 N, it was 3.2%.

Conclusions

1. Bio-ethanol is obtained with 3 steps: hydrolysis, fermentation and distillation process. The process of hydrolysis at 90 °C and HCl concentration of 0.3 N resulting the greatest levels of bio-ethanol, which is 61.20%.

2. The greater the temperature hydrolysis, the levels of produced bio-ethanol greater.

3. The greater the temperature hydrolysis, the yield of produced bio-ethanol greater.

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