Increasing Bioethanol Content From Pineapple Skin Using Catalyst Waste as Adsorben Results from Cracking Process in PT. PERTAMINA RU III

Kiagus Ahmad Roni*, M. Burhan Yusuf, Indra Pratama, Mita Yulia Kurniati, Netty Herawati

Chemical Engineering Department, Muhammadiyah Palembang University, Jalan Jendral Ahmad Yani 13 Ulu, Palembang, Indonesia

Correspondent author e-mail: kiagusaroni@gmail.com

ABSTRACT

Bioethanol is an ethanol produced from fermentation that has passed the distillation results. One of the raw materials that can be used to make bioethanol is pineapple skin. Sugar content contained in pineapple skin is 11.40%. From the fermentation process using bread yeast the resulting bioethanol content is 4,5%. To increase the bioethanol produced, other methods besides distillation are used, namely the adsorption process. The adsorbent used in this study is Pertamina RU III waste cracked. The use of this type of adsorbent is as a substitute for natural zeolite adsorbents which are more relatively expensive than Pertamina RU III wasted cracked that is easily to get and more economical. The purpose of this research is to find out how to increase bioethanol using this type of adsorbent. The result of this research is increasing contents of 65,855% with physically activated.

Key words : Bioethanol, Adsorpstion, Pertamina RU III Cracking Catalyst Waste.

1. INTRODUCTION

The energy crisis is a very basic problem in Indonesia. In modern life, energy can not be separated from daily life. The high dependence on fossil fuels, especially petroleum (about 47%), coal (27%) and natural gas (20%) has resulted in the depletion of fossil fuels. Fossil resources are non-renewable and for long term natural resources will eventually run out if explored continuously. So it is necessary to develop renewable energy such as Poernomo's ethanol productivity, (2014).

According to Andayana, (2014) a problem often faced in the chemical industry is the use of cheap useless materials into more useful and high-value materials. Alcohol can be produced from plants that contain lots of cellulose compounds using the help of microbial activity. The use of alcohol, especially ethanol as fuel, is one of the solutions to energy problems today. Because we know the use of energy (especially petroleum) from year to year is greatly increasing. While the source of fuel in use is running low, so we need another alternative to find a new fuel source.

Bioethanol is ethanol which is produced from the fermentation of glucose (sugar) followed by the distillation process. The distillation process can produce ethanol at 95% by volume, to be used as fuel (biofuel), it needs to be refined more until it reaches 99%, commonly called Fuel Grade Ethanol (FGE). The purification process with the principle of dehydration is generally carried out by the Molecular Sieve method, to separate water from ethanol compounds (Musanif, 2012).

Ethanol is categorized into two main groups, namely: Ethanol 95-96%, called "hydrated ethanol", which is divided into, Technical / raw spirit grade, used for spiritus fuels, drinks, disinfectants, and solvents. Industrial grade, used for industrial raw materials and solvents. Potable grade, for high quality drinks. Ethanol with levels > 99.5%, is used for fuel. If further purified it can be used for pharmaceutical and solvent purposes in the analysis laboratory. There is also in making bioethanol the basic ingredients used must have several requirements, namely: containing sucrose (succrose), generally used molasses (drops) from cane sugar, containing starch (amylum) and can also come from grains or plants, and can be derived from hydrocarbon gases and also from materials containing cellulose (cellulose) and waste materials from agricultural products.

Chemical reaction of the formation of ethanol from sucrose by fermentation as follows:

 $\longrightarrow C_{12}H_{22}O_{11} + H_2O \qquad C_6H_{11}O_6 + C_6H_{12}O_6$ $C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$

Glucose (sugar) is one of the main raw materials for the fermentation process. Glucose is found in plants that contain sugar such as sugar cane, sweet potatoes, bananas, etc. One of the plants that contains glucose is pineapple.

According to Murniati (2010) Indonesia in general only develops two classes of pineapple, namely Cayenne which has fine leaves, thorny to thorny, large fruit size, cylindrical, rather flat fruit eyes, yellowish green, and tastes slightly sour. As well as the Queen group that has the characteristics of short leaves and sharp spines, oval-shaped fruit like a cone to cylindrical, fruit eyes protruding, reddish yellow and sweet taste.

At this time many Indonesian people only consume the flesh and the rest is thrown away. Even though the pineapple fruit skin still contains meat which can be used as raw material for making Bioethanol. Pineapple skin contains active substances including anthocyanins, vitamin C and flavonoids. In addition there are bromelin and tannin enzymes (Caesarita, 2011).

In addition to the flesh according to the proximate pineapple fruit skin analysis of Harahap (2014), it contains 86.70% water, 0.69% protein, 0.02% fat, 0.48% ash, 1.66% Wet Fiber, and Kabohhid 10.54%. Based on the above analysis it can be seen that pineapple skin has the potential to become a raw material in the manufacture of bioethanol.

The activity of breaking down sugar (carbohydrates) into ethanol compounds by releasing CO2 gas is called fermentation. Fermentation is the change of one material to another with the help of microorganisms. These microorganisms in the form of plants that do not have chlorophyl, namely yeast and mold bacteria. These microorganisms eat organic material, therefore food is an important factor in the fermentation process and because of changes in certain substances (nutrients), the microorganisms can grow and multiply and change food ingredients into other materials. Fermentation is also an oxidation reaction or reaction in a biological system that produces energy where the donor and the acceptor are organic compounds. Organic compounds that are commonly used are sugars. The compound will be changed by the reduction reaction with the enzyme catalyst into another compound. This fermentation is carried out under anaerobic conditions. The most bioethanol production uses anaerobic Saccharomyces Cerevisiae microbes are Saccharomyces Cerevisiae. This microbe can be used for the conversion of sugar into ethanol because of its good conversion ability. However, it should be noted also the pH during fermentation because according to Winjayana (2011) at high pH the lag phase will decrease and fermentation activity will rise.

The conditions for obtaining a good fermentation process are: Microorganisms must produce the desired product, must be fast-multiplying and can maintain their uniform biological characteristics. The basic material (raw material) as a place to live must be cheap and the results must be useful. Fermentation must occur quickly and the substances produced must be easily purified. There are also factors that must be considered in the fermentation process are as follows: Microorganisms, equipment and the process itself. The degree of acidity (pH), the fermentation temperature must be based on the ambient temperature with a maximum ambient temperature of 40 $^{\circ}$ C, aeration (giving air), stirring and pure culture. Besides organic food, it also requires other substances such as persulfate, ammonium phosphate.

Based on previous studies Astuti, et al (2012) purified bioethanol using the adsorption method using adsorbents from natural zoelit and limestone by comparing the physical and chemical activations. And from the results of research conducted obtained the highest increase in bioethanol by 27.22%.

Adsorption is a process that occurs when a fluid (liquid or gas) is bound to a solid and finally forms a film (thin layer) on the surface of the solid Saputra, (2008). The adsorption process is usually carried out by contacting the solution or gas with solids, so that some component of the solution or gas is absorbed on the pore surface of the solid, consequently it will change the composition of the solution. The material used to carry out the adsorption process is called adsorbent, while the material called adsorbate. A good adsorbent must have the capacity and selectivity of adsorption of the adsorbate molecule.

Some factors that affect absorption on the surface of solids are: Type of polarity of adsorbates, generally adsorbates are ionic with high polarity, if the diametem is proportional then polar molecules are absorbed stronger than non-polar molecules. Type of bond, unsaturated compounds are better absorbed when compared to saturated compounds. Temperature, temperature also affects adsorption. In physical adsorption, the increase in temperature causes adsorption to decrease. This is due to the mobility of the atoms of an adsorbed substance which increases with increasing temperature.

Therefore, the absorbed substance tends to leave the absorbent, whereas in chemical adsorption, adsorption increases with increasing temperature. An increase in temperature can also cause the adsorbent pores to open more because impurities on the surface will oxidize. pH, Adsorption between the solid-liquid phase is strongly influenced by the pH of the solution. Adsorption carried out at high pH tends to give less than perfect results, because in alkaline conditions formed oxide compounds from larger impurities so that it will cover the surface of the adsorbent. Contact time also affects the ability of absorption. Ability of absorption increases with the length of time of contact between the adsorbent and adsorbate until it reaches equilibrium.

To be used as an adsorbent that can absorb well, the adsorbent must be activated first. Activation of adsorbents can be done in two ways namely physically or chemically. The way physics is done by heating, Chemical activation is done by acid or base, the following explanation of the process of activation of adsorbents: Activation of Physics, Activation of physics is usually done by heating which aims to vaporize the water trapped living in the pores of the adsorbent, so that the surface area adsorbent increases. Adsorbents that are heated at high temperatures cause the water molecules contained therein to become dehydrated. The dehydration properties of this catalyst affect the adsorption properties. Heating is carried out in a furnice at a temperature of 300°C (for laboratory scale) for 3 hours. Chemical Activation, Chemical activation is carried out with an acidic or basic solution, with the aim of cleaning pore surfaces, removing impurities, and rearranging the location of interchangeable atoms. Activation of adsorbents with acids causes the neutralization of negative charges on the cathals surface. The acids that can be used for activation are HCl, HNO3, H2SO4, and H3PO4. Among these acids the most effective for dealumination is HCl. Adsorbent activation is done to increase the adsorption capacity and obtain the desired catalyst properties. In the initial state, the adsorbent has a low adsorption ability but through activation (acid addition and heating) the adsorption power will increase.

Natural zeolite is one of the adsorbents used by Astuti, et al (2012) in his research. Natural zeolite is a porous material with good physicochemical properties, such as high cation exchange capacity, cation selectivity and large pore volume. However, the use of natural zeolites can potentially damage the environment and therefore an alternative use of adsorbents, namely Katils bekasi resulting from cracking petroleum. Cracking is the process of breaking down large hydrocarbon compound molecules into small hydrocarbon compound molecules.

The use of catalysts used in the cracking process itself was inspired by the research of Handono, (2017) who made use of this waste. Therefore the purpose of this study is to reduce industrial waste with more useful uses. In addition to reducing waste from the use of catalysts used in the cracking process is also far more economical, because the waste itself is obtained free of charge from Pertamina RU III Plaju.

2. METHOD

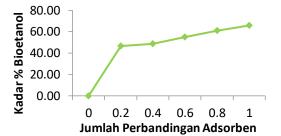
The raw material for pineapple skin used is the Queen type pineapple obtained from the plaju market in the sub-district of plaju, palembang. And for microorganisms to convert glucose into ethanol is Saccharomyces Cerevisiae. With the addition of aluminum sulfate and urea as nutrients for these microorganisms. Fermentation occurs at room temperature (20oC-30oC) with the pH set at 4-5. The fermentation results are then distilled at 80oC.

The adsorbent obtained from pertamina RU III, is first mashed with a size of 100 mesh and then activated physically in the furnace at 200°C, 250°C, and 300°C for 3 hours. For the adsorption process itself, the adsorbent used was added with bioethanol in a ratio of 1: 0.2, 1: 0.4, 1: 0.6, 1: 08, 1:1 using the ratio based on research by Safitri, et al (2014).

3. RESULT

The result of bioethanol fermentation from pineapple skin that has been purified by the distillation process is 4.5%. As for the results of the increase with the adsorption process can be seen through the following graph.

Figure 1: Comparison of the number of adsorbent ratios used with bioethanol produced at 200°C



In figure 1 above, it can be concluded that the highest purification obtained is by the use of a lot of ratio of bioethanol and adsorbent 1:1 with activation temperature of 200° C. Where the percentage obtained is 55,738% with 120 minutes of operating time with an initial bioethanol level of 4.5%.



Figure 2: Comparison of the number of adsorbent ratios used with bioethanol produced at 250°C.

In figure 2 it can be concluded that the use of an amount of adsorbent with activation temperature greater than before was 250°C with a comparison of bioethanol with adsorbent 1:1. Where the highest percentage results obtained were 59,107% with 120 minutes operating time with initial bioethanol levels 4.5%.



Figure 3: Comparison of the number of adsorbent ratios used with bioethanol produced at 300°C.

In figure 3 it can be concluded that the amount of bioethanol obtained increases from the previous activation temperature. At 300°C, an increase of 65.855% was seen. With a comparison of bioethanol and adsorbents 1:1. With an operating time of 120 minutes with an initial level of 4.5%.

From the results of these graphs it can be concluded that the use of adsorbents from the former cracking catalyst waste shows changes that are fairly linear. From bioethanol levels before adsorbed 4.5% increased by 61,355% at 300°C. Figure 3 shows that the best adsorption occurs when the more adsorbents used, the better the increase in bioethanol.

This is because adsorption occurs due to contact between the surface of the solid (adsorbent) and solution (bioethanol), so that some components of the solution are absorbed on the pore surface of the solid, consequently it will change the composition of the solution. The treatment of wasting also affects the absorption process because the treatment of wasting the surface area of the particles will be even greater, this also increases the ability of absorbents to absorb water in bioethanol.

The reduction in particle size also indirectly plays a role in the absorption of this adsorption process because according to the literature the smaller the particle size of the adsorbent, the more surface area of the adsorbent. Because the more surface area, the more ethanol contact with adsorbent, so that more water is absorbed and the adsorption can run optimally. In addition, the smaller the adsorbent particle size, the greater the adsorption velocity Prayitno, et al., (2009).

The temperature contributes greatly to the activation in physics because by heating the pores in the cracking former catalyst will increase. The cracking catalyst that has been furnished at high temperature will become dehydrated. And the nature of dehydration is what influences the adsorption process. This is like the literature of Rahayu et al (2014) the higher the temperature and the longer the contact time, the better the adsorbent absorption.

4. CONCLUSION

Based on research that has been done, it can be concluded that the increase in bioethanol with the physical adsorption method is best at a temperature of 300°C and with a ratio of bioethanol with adsorbent 1:1. With an increase of 61,355% with bioethanol before an increase of 4.5%. The adsorbent used is catalyst waste from cracking pertamina RU III plaju has the potential to be an adsorbent in the purification of bioethanol. However, it is necessary to do further research with a greater number of variables in order to find out the optimal point of the current study.

REFERENCES

- 1. Amelia, R. 2003. Pengaruh Konsentrasi Molekul Pengarah Terhadap Kristalinitas dan Komposisi Mineral Zeolit pada Modifikasi Zeolit Alam Wonosari. Semarang : UNDIP.
- 2. Flanigen, E.M. dan Khatami. 1971. *Infrared Structural Studies of Zeolite Frameworks*. New York : Union Carbide Corporation.
- 3. Ismaryata. 1999. The Study of Acidic Washing Temperature and Calcination Effect on Modification Process of Natural Zeolite as an Anion Exchanger. Semarang : Universitas Dipenegoro.
- 4. J.I Hurtes, N. Giraldo and S.Izquierdo. *Removal of H₂S and CO₂ from Biogas by Amine adsorption*. Meksiko.
- 5. Pertamina. 2018. "Material Safety Data Sheet". Plaju : Pertamina RU III.
- 6. Pertamina. 2018. *TKI Pengenceran Caustic Dan DEA pada Unit Purifikasi*. Plaju : Pertamina RU III
- 7. Saleh, Abdullah., Rera Oktariya, dan Yuni Aviva Sarah. 2017. Pengaruh Massa Zeolit dan Laju Alir Compressed Natural Gas Terhadap Peningkatan Metana Melalui Proses Pemurnian. Unsri Jurnal Teknik Kimia Vol. 23, No. 2.
- 8. Sigot, Lea., Gaelle Ducom, Patrick Germain. 2015. *Adsorption of Hydrogen Sulfide (H₂S) on Zeolite (Z) : Retention Mechanism*. Prancis : Universite de Lyon.
- 9. Sutarti, M dan Rachmawati. 1994. Zeolit Tinjauan Literatur. Jakarta : Pusat Dokumentasi dan Informasi Ilmiah LIPI.
- 10. Weller, M. T. 1994. Inorganic Materials Chemistry. Oxford : : Oxford University Press.
- 11. Widhiyanuriyawan, Denny dan Nurkholis Hamidi. 2013. Variasi Temperatur Pemanasn Zeolit Alam NaOH Untuk Pemurnian Biogas. Malang : Jurnal Energi Dan Manufaktur Vol. 6, No. 1.