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Autocatalytic Hydrolysis of Palm Oil for Fatty Acid **Production by Using Hydrothermolysis Process**

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Abstract. As the world major leader in the palm oil production, Indonesia need to develop a new efficient technology to replace the conventional production process of fatty acid from palm oil. Auto catalytic hydrolysis reaction of palm oil in a hydrothermal reactor offers several benefits in fatty acid production. This research objective was to determine the rate constant of hydrothermal auto catalytic hydrolysis reaction of palm oil in fatty acid production. The Auto catalytic hydrolysis reaction of palm oil was conducted in several reaction temperatures (130-150°C) at a different time (5-30 minutes). The research results show that at all the temperature applied, along with the increasing of reaction time, the fatty acid obtained were increasing also, while the highest fatty acid concentration was obtained from the auto catalytic hydrolysis reaction of palm oil performed at temperature of 130°C.

1. Introduction

Nowadays, Indonesia is being the world leader in the production of crude palm oil in which the palm oil production share is reach of 48%, and followed by Malaysia in which the palm oil production share is reach of 37% from the global palm oil production rate. Nonetheless, Indonesia is still improrting fatty acid and its derivats wherein commonly utilized inf paint industry, plasticsm cosmetics, deteregents, soap, and food industries such as chocolate, ice cream, candy and bakery. This unfortunate condition has to be solve for fulfill the national demand of fatty acid. The main reason for the lack of fatty acid in Indonesia was due to the in economical production process of fatty acid.

Colgate-emery process was the conventional method applied for fatty acid production in Indonesia. This process is considered as an in economical process since the hydrolysis time is very long, the conversion is relatively low and the purification section was a heavy duty one due to the application of acid catalyst. Several enzymatic fatty acid production scheme were patented ie. U.S. Paten No. 4.208.432; U.S. Paten No. 5.518.754; and U.S. Paten No. 6.706.502¹⁻³. Nonetheless, the conversion is lower than the Colgate-Emery conversion. The basic drawbacks of this process sheme based on the patented ones were: (i) the heavy duty of the purification section due to the low level of fatty acid in which lower than 80%, (ii) lipase enzyme is undergo instability and inactivation, and (iii) the low productivity due to the long of residence time. Furthermore, considering the high value of fatty acid, then the search for the methods for fatty acid production is need to be done. The development of hydrothermal auto catalytic hydrolysis reaction of palm oil for fatty acid production was one of a potential solution.

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The hydrothermal auto catalytic hydrolysis reaction in fatty acid production was efficient since subcritical water could asts as reactant, solvent⁴⁻⁵ and as catalyst⁶. Nonetheless the application of this method was hindered by the finding of the optimum process condition, hence subcritical water was able to fasten the rate of hydrolysis reaction, hence the research was focusing to hydrothermal auto catalytic hydrolysis and determined the rate constant and the mathematical model of hydrothermal auto catalytic hydrolysis reaction.

Current knowledge on conversion in subcritcal water still spreading without a consistent picture⁷. The novelty and the basic innovation of this research were the utilization of auto catalysis hydrotermolysis on the fatty acid production from palm oil in which having several benefits over the other conventional process i.e: (i) the utilization of subcritical water in which has three parallel function i.e as reactant, reaction solvent, and catalyst, (ii) this process was able to fill the drawback of *Colgate-Emery* process since the utilization subcritical water will increase the process efficiency by fastening the hydrolysis reaction time with high yield and lowered the production cost by omitting the purification steps, (iii) the process was able to fill the enzymatic process drawbacks such as the long the retention time and the high cost of the enzyme, (iv) subcritical water able to lowered the activatoion energy and produce large amount of hidronium ion (H₃O⁺) in which further acts as catalyst thus reduce the production cost, (v) subcritical water could act as reaction medium in hydrolysis reaction thus increase the opportunity of homogeny phase, (vi) the simple process and only need control of water temperature, process time and pressure.

2. Methods

Research on the autocatalytic hydrolysis of palm oil in a hydrothermolysis reactor was investigated experimentally. The research steps were comprised of autocatalytic hydrolysis of palm oil in a hydrothermolysis reactor, product cooling step and product analysis. Materials utilized for this research were palm oil and chemicals for analytical purposes i.e for volumetric determination of acid number. Meanwhile glasswares were utilized for the titration for acid number determination.



Figure 1. Hydrothermal autocatalytic hydrolysis reactor

The autocatalytic hydrolysis was conducted by varying the temperature $(130-150^{\circ}C)$, in which their kinetics energy of those temperature range exceed the activation energy of the sub critical phase, and by varying the time of the hydrolysis process (5-30 min). 2000 ml of palm oil was fed to the covered stainless chamber and placed into the autocatalytic hydrolysis reactor. 2 L of distilled water was added to the reactor and then the reactor was covered with the stainless cover and sealed. Nitrogen was fed inti the reactor for 2 minutes in order to omit the air and oxygen. Excess of pressure was purge through the valve and the reactor temperature was set on a certain value according to the research variables. It took 3-5 minutes to reach the desire temperature and then the autocatalytic hydrolysis was started (t = 0). All the experiments were conducted at a certain pressure. After the autocatalytic hydrolysis was completed, the hydrothermolysis products was transferred to the cooling cell in which having temperature of 25°C, and pressure of 1 Mpa for 1 minute for an instant cooling. Along the autocatalytic hydrolysis, samples were taken in every 5 minutes for further analysis purposes. Fatty

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acid compositions were determined by applying GC. The conversion factor was calculated based on the obtained fatty acid to the initial weight of palm oil used. The free fatty acid was calculated base on its acid number.

3. Result & Discussion

Figure 2 represents the fatty acid obtained form the autocatalytic hydrolysis of palm oil in a hydrothermolysis reactor performed at temperature of 130°C as time function. Along with the increasing of reaction time, the fatty acid is getting higher. It was logical since the longer the reaction time, the higher the possibility of the reactant molecules to collide in which catalyzed by the hydronium ion (H₃O⁺), thus lowered the activation energy. Water at temperature of 130°C and pressure of 2 bar was at its subcritical condition and could act as catalyst since it has a large amount of ion as a result of water ionization process. The hydrogen bond of water at temperature of 130°C was getting weaker, hence results in the autoinization of water and produces hidronium ion (H_3O^+) in which function as acid catalyst. Furthermore, along with the longer the reaction time, the more the amount of triglyceride converted into fatty acid. This phenomenon was in accordance to the Ruiz (2013) in which stated that in the temperature higher than 150°C the hydrogen bond of water is getting weaker thus results in the autoinization of water and produces hidronium ion (H_3O^+) in which function as acid catalyst and also produce of hydroxide ion (OH⁻) in which acts as base catalyst. In the meantime, subcritical water can also low the activation energy. Sasaki et al (2003) in Peterson et al (2008) reported that the cellulose degradation kinetics is faster when subcritical water is applied, in which associated with the activation energy inclining from 146 to 548 kJ/mol when the temperatur exceed of 370°C. Autocatalytic hydrolysis in a hydrothermal reactor is a liquid phase reaction in which the temperature was set at temperature range of 100-374°C at a certain pressure wherein the water was called as in subcritical condition⁸.



Figure 2. Fatty acid obtained from autocatalytic hydrolysis conducted at temperature of 130 °C Figure 3 and 4 illustrated the fatty acid obtained from autocatalytic hydrolysis conducted at temperature of 140 °C and 150 °C as time function. The longer the reaction time, the higher the fatty acid obtained. It was due to that subcritical water in hydrolysis reaction could act as reactant, reaction solvent⁴⁻⁵ and as catalyst ⁶. As reactant, subcritical water could form a new formation of covalent bond with the OH units by the organic moldecules transformation, reaction in which reacts with water. Sub critical water could also act as hydrolysis solvent since subcritical water having higher oil solubility and the dielectric constant decreased along with the increasing of temperature ⁹⁻¹¹. As hydrolysis medium, subcritical water will increase the opportunity of the homogeneous reaction while if the reaction was proceed in conventional operation condition, thus the reaction will proceeed on heterogeneous phase ¹².



Figure 3. Fatty acid obtained from autocatalytic hydrolysis conducted at temperature of 140 °C

Hydrolysis reaction of autocatalytic hydrothermal was also catalyzed by the free faty acid liberated from the hydrolysis reaction. Morechi et al., (2006) mentioned that hydrolysis using subcritical water or known as hydrothermolysis was initially catalyzed by hydronium ion resulted from the autoionization of water and then followed catalysis reaction by fatty acid from the reaction¹³. Alenezi et al., (2010) and Milliren et al., (2013), stated that when the fatty acid liberated from the hydrolysis reaction, the fatty acid will act as catalyst¹⁴⁻¹⁵. Alenezi et al. (2010) reported that free fatty acid acts as acid catalyst and thus proceed as a simple process and high yield of fatty acid was obtained¹⁴. Subcritical water was proved as an effective medium and catalyst in corn oil hydrolysis in which the yield obtained was 90% for 8 minutes of reaction, water oil ratio of 50:50 v/v, temperature of 350°C at a certain pressure.





temperatures. It can be seen that along with the increasing acid number, the fatty acid obtained were increasing also. This phenomenon was conceivable since in temperature higher than 130° C, the hydrogen bond of water is become weaker and thus produce an autoionization of water and producing hydronium ion (H₃O⁺) wherein could acts as acid catalyst. This phenomenon was in accordance to the Ruiz (2013) in which stated that in the temperature higher than 150° C the hydrogen bond of water is getting weaker thus results in the autoinization of water and produces hidronium ion (H₃O⁺) in which function as acid catalyst and also produce of hydroxide ion (OH⁻) in which acts as base catalyst¹⁶. The ionization constant (K_w) of subcritical water was also increase along with the increase of temperature¹⁶. The high number of ionization produc of subcritical water was due to the weakness of the hydrogen bond in water at temperature of higher than 150° C¹⁷.

International Conference of **IOP** Publishing 1.80 IOP Conf. Series: Material 1757-899X/1053/1/012065 160 140 120 Acid number 100 T=130C \$0 T=140C 60 T=150C 40 20 0 40 0 10 20 30 Time (minutes)

Figure 5. Fatty acid from autocatalytic hydrolysis conducted at various temperature

4. Conclusion

The research results show that at all the temperature applied, along with the increasing of reaction time, the acid number that generate fatty acid value recorded were increasing also, while the highest fatty acid concentration was obtained from the auto catalytic hydrolysis reaction of palm oil performed at temperature of 130°C.

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