Preliminary study of auto catalytic palm oil hydrolysis into fatty acid through hydrothermalysis process

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Abstract. This research aims to carry out the production of fatty acids through hydrothermal autocatalytic hydrolysis of palm oil. The production of commercial fatty acids is the hydrolysis of crude palm oil which is carried out using the Colgate-Emery process. This process is considered to be less efficient because the hydrolysis time is quite long, the conversion is relatively low and the product purification load is more complex in the presence of an acid catalyst. Hydrothermal autocatalytic hydrolysis is a liquid phase reaction which is maintained at a temperature of 100-374°C under certain pressure or referred to as subcritical water. Research on the forming of fatty acids through autocatalytic hydrolysis of palm oil in a hydrothermal reactor was investigated experimentally. The research variables varied were temperature and reaction time. To conclude, as the reactor temperature increases and the hydrothermal reaction time is longer, the number of acids obtained increases, meaning that the fatty acids produced through the autocatalytic reaction get bigger.

1. Introduction

At present, Indonesia has become the largest palm oil producer in the world, at 48%, followed by Malaysia at 37% of the total volume of world palm oil production. However, Indonesia still imports fatty acids (CPO derivatives) used in the paint, plastics, cosmetics, detergent and soap industries and food products such as the chocolate industry, the ice cream industry, the pastry industry, and the candy industry. This is unfortunate, so it is necessary to take a step in the fulfilment of fatty acids for domestic needs. The main cause of the lack of fatty acids in Indonesia is because the manufacturing process is considered uneconomic.

In Indonesia, the production of commercial fatty acids is the hydrolysis of crude palm oil which is carried out using the Colgate-Emery process. This process is considered to be less efficient because the hydrolysis time is quite long, the conversion is relatively low and the product purification load is more complex in the presence of an acid catalyst. Several schemes of enzymatic production of fatty acids have also been patented, including U.S. Patent No. 4,208,432; U.S. Patent No. 5,518,754; and U.S. Patent No. 6,706,502 [1-3]. However, the resulting reaction conversion is still under the Colgate-Emery process. The basic disadvantages of the process scheme such as the patent above are: (i) the purification burden is very high because the concentration of fatty acids is less than 80%, (ii) the lipase experiences instability and inactivation, and (iii) low productivity, due to the relatively long residence time. However, given the high economic value of fatty acids, it is necessary to find an alternative solution. The development carried out is the production of fatty acids through hydrothermal autocatalytic hydrolysis of palm oil.
Hydrothermal autocatalytic hydrolysis is a liquid phase reaction which is maintained at a temperature of 100-374°C under certain pressure or referred to as subcritical water [4-6]. The strength of subcritical water in the hydrolysis reaction, because it is able to function as a reactant, reaction solvent [7-8] and as a catalyst [4]. As a reactant, subcritical water will produce a new covalent bond formation with OH groups by the transformation of organic molecules, RX that reacts with water.

The function of subcritical water as a hydrolysis solvent is because it has the characteristics of higher oil solubility and changes in physical properties of water, such as a decrease in the dielectric constant value of water with increasing temperature [9-11]. As a hydrolysis reaction medium, subcritical water will increase the chances of a reaction occurring in a homogeneous phase, whereas if the reaction is carried out under conventional operating conditions the reaction will occur in the heterogeneous phase [12]. Subcritical water functions as a catalyst because it has a higher number of ions resulting from the water ionization process. The ionization constant (Kw) of subcritical water also increases with increasing temperature [6]. The high number of subcritical water ionization products is caused by the weak hydrogen bonds of water at temperatures above 150°C [5]. Weak hydrogen bonds in water will result in the autoionization of water into hydronium ions (H3O+) which can function as an acid catalyst and hydroxide ion (OH-) which can function as a base catalyst [6]. In addition, subcritical water is able to decrease the activation energy [13]. Sasaki et al (2003) in Peterson et al (2008) reported an increase in degradation reaction kinetics cellulose by subcritical water, which is associated with a change in activation energy from 146 to 548 kJ / moles when the system is heated past 370°C [14].

The hydrothermal autocatalytic hydrolysis process is also catalysed by free fatty acids formed from the hydrolysis reaction. Morechi et al., (2006) stated that the hydrolysis process using subcritical water or known as hydrothermalysis was initially catalysed by hydronium ions from auto ionized water and subsequently provided by acids formed from the reaction results [15]. Alenezi et al., (2010) and Milliren et al., (2013), stated that when free fatty acids are formed from hydrolysis reactions, these fatty acids will act as acid catalysts and accelerate the hydrolysis reaction itself [16-17]. Alenezi et al. (2010) states that free fatty acids function as acid catalysts to produce simple processes with high yields [16]. Subcritical water has proven to be effective in hydrolysis of corn oil with yields reaching 90% for 8 minutes, oil-water ratio 50:50 v / v, temperature of 350°C at a certain pressure.

The autocatalytic hydrothermal hydrolysis technique for the manufacture of fatty acids is felt to be very efficient because subcritical water is able to function as a reactant, solvent and as a catalyst. However, the three functions of subcritical water are still constrained in optimum process conditions, so that the subcritical water is able to accelerate the rate of hydrolysis reaction. For this reason, the focus of research is directed to determine the rate constants of autocatalytic hydrothermal reactions in the form of mathematical models. The purpose of this study was to determine the rate constant of the autocatalytic hydrothermal reaction of palm oil to fatty acids through the hydrothermal process.

The fundamental novelty and innovation in this research is the use and development of the autocatalytic hydrothermal process in the production of fatty acids from palm oil has various advantages compared to conventional processes, such as (i) the use of subcritical water which has three functions at once namely as a reactant, a reaction solvent and catalyst, (ii) able to overcome the weaknesses of the Colgate-Emery process because the use of subcritical water will increase the efficiency of the process by accelerating the reaction time of hydrolysis with high yields and being able to reduce costs for the purification process, because without the catalyst, (iii) able to overcome the weaknesses of the enzymatic process i.e. it takes a relatively long residence time and the price of commercial enzymes is quite expensive, (iv) subcritical water can reduce activation energy and has a high amount of hydronium ion (H3O+) which can function as an auto catalyst so that it will reduce production costs because there is no need for the addition of catalysts, (v) sub-chemical water tis functions as a hydrolysis reaction medium so that it will increase the chances of a reaction occurring in a homogeneous phase, (vi) a simple process and only requires control of water temperature, processing time and pressure.
2. Methods
Research on the forming of fatty acids through autocatalytic hydrolysis of palm oil in a hydrothermal reactor was investigated experimentally. The series of studies carried out in stages include the autocatalytic hydrolysis reaction of palm oil in the thermolysis reactor, product cooling and product analysis. The raw material used in this study is palm oil. Other materials needed are materials to carry out titration in determining acid numbers to test the levels of free fatty acids. The main equipment used in this study is the autocatalytic hydrothermal hydrolysis reactor presented in Figure 1. Another device that is needed is a tool for the purposes of titration in the determination of acid numbers.

![Figure 1. Hydrothermal autocatalytic hydrolysis reactor](image)

The research variables varied were temperature and reaction time. The reactor temperature is set at 130, 140, and 150, because it is a range of temperatures with kinetic energy far surpassing the activation energy in the subcritical phase. The reaction time is set at 5, 10, 15, 20, 25 and 30 minutes. The feed or reactant in the form of 2000 ml of palm oil is put into a closed stainless steel tube and placed into an autocatalytic hydrothermalysis reactor. 2000 ml distilled water and varied to a certain ratio was added to the reactor. The reactor cell is closed with a stainless lid, N₂ gas is flowed into the reactor for 2 minutes to remove air and dissolved oxygen. The excess pressure is discharged through the valve. The temperature is set under certain conditions and heating takes 3-5 minutes to reach the desired temperature. The autocatalytic hydrothermal process begins (t = 0) when the temperature is reached under certain conditions. All experiments are carried out under certain pressure. After the process is complete, the hydrothermal product is transferred to the cooling cell at 25°C, 1 Mpa for 1 minute for a brief cooling. During the autocatalytic hydrothermalysis reaction, a number of samples are taken at any given time. Samples in the form of fatty acids, glycerol, water, and triglyceride residual acid numbers measured to determine the amount of free fatty acids.

3. Result and discussion
Figure 2 presents the fatty acids produced by autocatalytic hydrolysis at 140°C as a function of time. The longer the reaction time, the number of acids obtained is increasing, this shows the fatty acids produced are getting bigger. The longer the hydrolysis reaction causes the greater the chance of collision between the reactant molecules catalysed by the hydronium ion (H₃O⁺), which will reduce the activation energy. Water in subcritical conditions at a temperature of 130°C 2 bar pressure, can function as a catalyst because it has a higher number of ions resulting from the water ionization process. At 130°C, the hydrogen bonds in the water get weaker, so that it will cause autoionization of water into hydronium ions (H₃O⁺) which can function as acid catalysts. Therefore, over time the hydrolysis reaction causes oil triglycerides to be converted to fatty acids getting bigger. This is in accordance with Ruiz's statement (2013) that temperatures above 150°C hydrogen bonds in water are
getting weaker so that it will cause autoionization of water into hydronium ions (H$_3$O$^+$) which can function as acid catalysts and hydroxide ions (OH) which can function as catalysts base$^6$. In addition, subcritical water can reduce the activation energy$^{13}$. Sasaki et al (2003) in Peterson et al (2008) reported an increase in the kinetics of cellulose degradation reaction by subcritical water, which is associated with the change in activation energy from 146 to 548 kJ/moles when the system heated past 370°C$^{14}$. Hydrothermal autocatalytic hydrolysis is a liquid phase reaction which is maintained at a temperature of 100-374°C at a certain pressure or referred to as subcritical water [4-6].

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Figure 3 presents the acquisition of fatty acids at various temperatures (130, 140 and 150°C) at 10 and 15 minutes. The greater the temperature of fatty acids produced is increasing. This occurs at temperatures above 130°C, the hydrogen bonds in the water get weaker, so that it will result in the autoionization of water into hydronium ions (H$_3$O$^+$) which can function as acid catalysts. This is in accordance with Ruiz’s statement (2013) that temperatures above 150°C hydrogen bonds in water are getting weaker so that it will cause autoionization of water into hydronium ions (H$_3$O$^+$) which can
function as acid catalysts and hydroxide ions (OH\(^{-}\)) which can function as catalysts base [6]. The ionization constant (\(K_w\)) of supercritical water also increases with increasing temperature\(^6\). The high number of supercritical water ionization products is caused by weak hydrogen water bonds at temperatures above 150°C [5].

![Graph showing effect of acid value and temperature](image)

**Figure 3.** Effect of acid value and temperature at 10 and 15 minutes

### 4. Conclusion

As the reactor temperature increases and the hydrothermal reaction time is longer, the number of acids obtained increases, meaning that the fatty acids produced through the autocatalytic reaction get bigger.

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