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Microwave-assisted Esterification Reaction of Free Fatty Acids from *Ceiba Pentandra* Seed Oil

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ABSTRACT

Ceiba Pentandra Seed oil, a non-edible feedstock, was used for biodiesel production. As this oil has high free fatty acids (FFA), H_2SO_4-catalyzed esterification with methanol was conducted to reduce the FFA content and to obtain a high-quality product in the next step. Microwave irradiation can facilitate the esterification reaction by reducing reaction time from hours in conventional heating to only few minutes while attaining high conversion of FFA. Under the reaction conditions of 2wt% of sulfuric acid and 10:1 methanol to oil molar ratio, more than 90% conversion of esterification was achieved in 12 minutes by microwave heating, while it took about 1 hour by conventional heating. Moreover, with the kinetic effect, this esterification reaction has been proven to be endothermic. A comparative study on esterification reaction at three different temperatures (50^oC, 60^oC and 70^oC) gave good results with the assistance of microwave, resulting in diminishing energy requirements to 3.6×10^5J, compared with 1.08×10^7J in conventional method. Microwave irradiation is an innovative method for biodiesel production.

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INTRODUCTION

Biodiesel:

The rapidly growing demand for energy, uncertainty about the costs and supply of petroleum and concerns about increasing greenhouse emissions by the use of fossils fuels have led to intense international interest in developing alternative non-petroleum fuels for engines. It is reported that the demand for energy will be 53% increase by the year 2030 (Shahid and Jamal, 2011). Biodiesel is one of the most sustainable and green energy resources. It has the potential to minimize pollution from the transport industry which is a significant contributor to global warming through emission of carbon dioxide. Biodiesel is a mixture of mono alkyl ester of long chain fatty acids derived from renewable biological sources such as vegetable oils, animal fats, waste cooking oil, and algae oil (Fogler, 2006). Among several procedures that include transesterification, blending, cracking, micro-emulsification, and pyrolysis have been applied to convert oils into fuels, transesterification emerges as the easiest used method for the development of better quality biodiesel.

The use of virgin vegetable oils for biodiesel production has a negative impact on the global imbalance to the market demand and the food resource by their high prices, the reduction of food storage and the growth of commercial edible oil crops' plantations. On the other hand, non-edible oils are grown in wastelands, which are widely available and further benefits as green cover to wastelands. Among these, *Ceiba Pentandra* emerges as a non-edible plant, containing about 22-25% (wt/wt) of oil in its seeds, which meets the requirement for current state (Salimon and Kadir, 2005).However, most of non-edible feedstocks contain high levels of free fatty acids (FFA) which cause severe deterioration of production efficiency. Therefore, the esterification step has received much attention since it reduces the concentration of free fatty acids with employing acid catalysts, improving the final yield in fatty acid alkyl esters.

Mechanism for esterification reaction:

In the esterification of FFA with methanol, concentrated sulfuric acid acts as a proton donor, increasing the rate of reaction between two reactants. This reaction mechanism has six steps as described

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in Figure 1. In the initial step, a proton from sulfuric acid is transferred to carbonyl oxygen, increasing the electrophilicity of the carbonyl carbon atom. The following step is the nucleophilic oxygen atom attack of the alcohol to that carbonyl carbon atom. Then proton transfer from the oxonium ion to a second molecule of the alcohol forms a complex conglomerate. This arrangement of atoms and charge is not stable, so it undergoes a protonation of one of the hydroxyl groups to give a new oxonium ion. Leaving of water molecule from this oxonium ion gives increased stabilization. Finally, deprotonation of sulfuric acid completes the process, producing the ester. Since concentrated sulfuric acid is regenerated but not degenerated by the reaction, it is considered as a mineral acid catalyst, not a reactant.

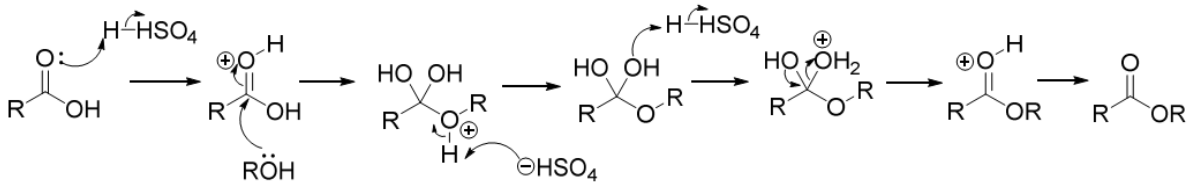

Fig. 1: Mechanism for esterification reaction (Loudon, 2009).

Microwave:

Discovered in 1946 by Dr. Percy, but it was not until 1986 with publications from Professor Richard Gedye and Professors Raymond J. Giguere and George Majetich that microwaves began to be employed in different areas of chemistry (Mazo and Rios, 2010). For chemical syntheses, microwaves have a wavelength of 12.25 cm, which corresponds to a frequency of 2.45 GHz. Microwave irradiation, an unconventional energy source, has been applied for a variety of chemical reactions because of its benefits such as short reaction time, cleaner reaction products and reduced separation-purification times (Gude *et al*., 2013). Microwavestransfer energy into materials by two mechanisms of dipolar rotation and ionic conduction. The energy interacts with the sample at the molecular level. This means microwaves manifests as heat by the interaction of the electric field of radiation with the matter that can affect molecular actions at a very fast rate, contributing to localized and rapid superheating of the sample(Gude *et al*., 2013; Sajjadi *et al*., 2014). This may lead to dramatic reduction of reaction time, improvement of process productivity and product purity. Compared with the wall heat transfer, microwave heating remains overwhelmingly dominant. In the conventional heating, heat is generated slowly and inefficiently because of convection currents and the thermal conductivity of the reaction mixture, resulting in non-uniform heating throughout the sample (Refaat and Sheltawy, 2008). In contrast, esterification under microwave irradiation is marked by even heating, short reaction time and being environmentally friendly for biodiesel production (Shi *et al*., 2010).

The aims of this study are to investigate the temperature effect of microwave irradiation on the esterification of *Ceiba Pentandra* Seed oil with high FFA catalyzed by H_2SO_4, to compare the efficiency between microwave heating and conventional heating as well as energy requirements for this reaction.

MATERIALS AND METHODS

Materials:

Methanol (99.9% purity) as solvent; acid catalyst H_2SO_4 (95 – 97%); titrant KOH pellet; drying agent Na_2SO_4 anhydrous (purity 99%) and qualitative filter paper were purchased from Merck Chemical Company (Darmstadt, Germany) and Sigma Aldrich Chemical Company (United States). All chemicals obtained were used without any further purification. *Ceiba Pentandra* Seed Oil was purchased from BUNGAKEMBANG ENTERPRISE CV in Indonesia.

Reaction setup:

The esterification of *Ceiba Pentandra* Seed Oil was conducted in a microwave synthesis reactor (MARS 6 SYNTHESIS, CEM Corporation PO Box 200, Matthews, NC 28106, United States) in a batch mode. In this process, a 500ml three-necked round-bottomed glass reactor was used. To prevent the loss of methanol during the reaction, a reflux condenser was fixed on the main neck of the flask. A mechanical stirrer was put inside the reactor for reaching a completely homogeneous mixture among the reactants at constant rate (Sivakumar *et al*., 2013).The maximum power for this type of glass was 500W. The power was automatically adjusted to the set temperature via a fiber optic probe which provided accurate measurement each time.

Acid-catalyzed esterification process:

Initially, fixed amount of crude oil was transferred to the flask. A known amount of sulfuric acid was mixed with preset quantity of methanol and the mixture was stirred thoroughly until sulfuricacid was completely dissolved. Then, the resulting catalyst solution was added to the oil and esterification reaction started until a certain period of reaction.

After completion of reaction, the products were poured into a separating funnel and allowed to cool down to separate the excess alcohol, acid catalyst and impurities presented in the upper layer for 24 hours. Then the esterified oil in the lower layer was

separated and washed with distilled water at 50°C to remove impurities, including sulfuric acid and methanol. Next, Na_2SO_4 anhydrous was added to eliminate water and filter paper was used to filter any traces of Na_2SO_4. Finally, the product was poured into a rotary evaporator set at 60°C under vacuum conditions for 1 hour to remove extra methanol and water.

In this study, the esterification was carried out at three different temperatures (50°C, 60°C, 70°C) and four different reaction time (2, 4, 8 and 12 minutes) using *Ceiba Pentandra* Seed Oil with the acid value 13.992mgKOH/g oil. Methanol to oil molar ratio at 10:1 and 2% mass fraction of sulfuric acid in oil were maintained during the process.

In order to determine the conversion of FFA during the process, the acid value of treated oil was analyzed to evaluate the reduction in the FFA content before and after esterification. The conversion of FFA was calculated as in reference (Man *et al*., 2013) using the following equation (1):

$$Conversion = \left(\frac{AV_i - AV_t}{AV_i}\right) x\, 100,\ \% \qquad (1)$$

Where AV_i is initial acid value of the mixture and AV_t is the acid value at any "t" time.

RESULTS AND DISCUSSION

Microwave-assisted esterification reaction:

As can be seen in Figure 2, with using 2wt% of H_2SO_4in oil and 10:1 methanol to oil molar ratio, the conversion of FFA was found to increase with the extension of reaction time. It was obvious that in the first two minutes, the FFA conversion rate was remarkably fast, and then slowed down gradually.The conversion for two minutes at 50°C, 60°C and 70°C was 77.31%, 84.26% and 86.41%, respectively.After twelve minutes, more than 90% of FFA was converted into methyl ester, which has been proven in previous papers that microwave irradiation is a fast method which rapidly reduces the FFA content within the first 15 min (Suppalakpanya *et al*., 2010).This is also evidenced by Kamath *et al*. (2011) in their work that the free fatty acids of crude Karanjja oil decreased to 87.39% in 190s under microwave irradiation using 3.73wt% of sulfuric acid and 33.83wt% methanol-oil ratio. In addition, it was observed that the FFA conversion rate increased considerably with an increase in reaction temperature and it reached the maximum conversion at 70°C in this study. Even though from 60°C to 70°C, there was a slight decreasein acid value of*Ceiba Pentandra* Seed Oil, it was still seen the trend of esterification reaction moving forward . This might be due to the fact that increasing the temperature apparently favours for the acceleration of the forward reaction as the reaction is endothermicunder a kinetically controlled regime, which has been also demonstrated in the work of Liu *et al*. (2013).From the theory of Le Chatelier's principle, for endothermic reactions, the equilibrium shifts to the right as the temperature increases (Fogler, 2006).

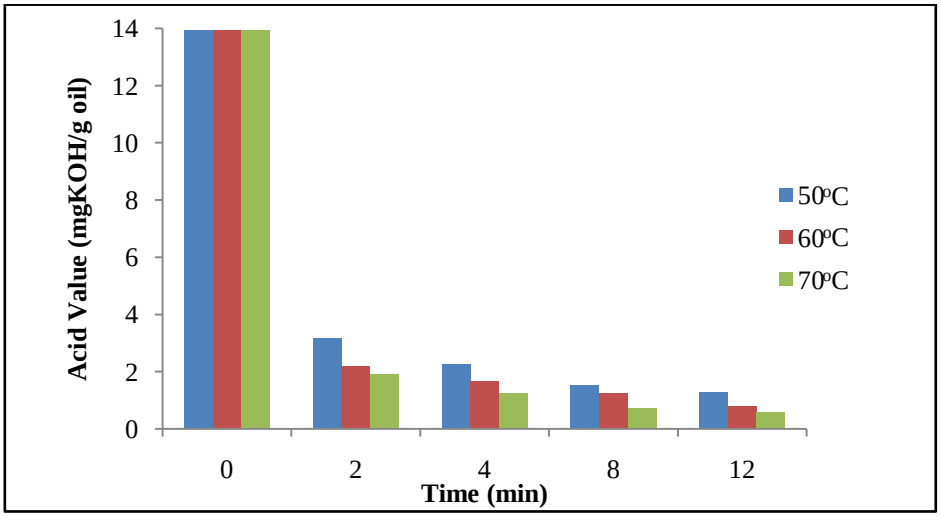

Fig. 2: Influence of temperature and reaction time on reduction of acid value in *Ceiba Pentandra* Seed Oil.

Microwave heating in comparison with conventional heating:

Table 1 describes the difference in optimum conditions for *Ceiba Pentandra*Seed Oil using microwave and conventional technique. As can be seen from the table, the FFA conversion can reach up to 94.43% in 12 minutes at 60°C with the assistance of microwave while it takes 60 minutes along using more amount of solvent to achieve 94.15% of FFA conversion in conventional method. On the other hand, to attain higher FFA conversion, longer time as well as higher temperature needs to be set in conventional method. Besides, in the work of Ahmad *et al*. (2014) using Rubber Seed Oil as the feedstock, to achieve more than 95% FFA conversion, 15:1 methanol to oil molar ratio, 10wt% of sulfuric

acidcatalyst, reaction temperature of 45°C were used in 90 minutes of reaction time. Through previous researches on conventional method for esterification reaction, again, microwave-assisted technique proved that it is an innovative method for chemical reactions, particularly in biodiesel production.

Table 1: Comparison of process variables with previous studies.

Parameters	Microwave			Conventional		
	This work			Ong *et al*. (2013)	Sivakumar *et al*. (2013)	Norazahar *et al*. (2012)
Temperature (°C)	50	60	70	60	65	65
Time (min)	12	12	12	180	60	180
Methanol to oil	10:1 (molar ratio)	10:1 (molar ratio)	10:1 (molar ratio)	10:1 (molar ratio)	8:1 (volume ratio)	6:1 (molar ratio)
H_2SO_4 Catalyst (wt%)	2	2	2	1.84	1.834	1
FFA conversion (%)	90.84	94.43	95.97	96.41	94.15	98.1

Comparison of energy demands between microwave heating and conventional heating:

It is evident that microwave heating is energy efficient as it reduces much reaction time for esterification process (Gude *et al*., 2013). Based on the paper of Wang *et al*.(2013), a very rough comparison of the power requirement can be obtained with the estimate of energy consumption (Q) involved in each type of heating. For microwave heating, the energy demand Q_M was determined to be 3.6×10^5J at maximum power 500W in 12 minutes. For conventional heating in the work of Ong *et al*.(2013), with maximum power 1000W in 60 minutes, the energy consumption was calculated to be 1.08×10^7J. Even with these rough estimates, it again does prove that the energy needed in microwave-assisted esterification is much less than that required in conventional heating.

Conclusion:

In this study, the esterification reaction from*Ceiba Pentandra* Seed Oil has been proven to be endothermic and microwave heating is efficient in facilitating the esterification of free fatty acids. Compared with traditional heating esterification, microwave-assisted esterification needed less reaction time (12 minutes) to convert more than 90% of FFA using 10:1 methanol to oil molar ratio and 2wt% of H_2SO_4. Furthermore, reaction time decrease led to reduce energy requirements for heating from 1.08×10^7J in conventional method to 3.6×10^5J in microwave irradiation. The results obtained were important to produce high-quality biodiesel in the transesterification process at shorter time.

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