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Biodiesel Production by Microwave Assisted Methanolysis of Refined Palm Oil in a Flow Reactor

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Abstract

Biodiesel is one of the most promising alternative fuels to reduce or even replace petroleum based diesel fuel. It offers many significant benefits, including being renewable, less greenhouse gas effect, low pollution, and non-toxic, while for the engine, biodiesel requires no modification and has excellent lubrication properties. Its production is potentially enhanced by combining the processes with microwave irradiation. Microwave does not only provide heating effect on the reactions, but also stimulate intermolecular interaction of involving materials such as reactants, solvent, and catalyst which is expected contributing on reaction rate enhancement. The purpose of this study is to produce palm oil biodiesel at a maximum yield in a short time by utilizing a flow reactor and microwave heating. The methanolysis was catalyzed by sodium hydroxide. The glass pipe reactor was installed inside a household type microwave. Flow rate of the reacting solution significantly determined the biodiesel yield. The yield was increased as the flow rate was reduced from 90 ml/min to 30 ml/min, and the yield was significantly dropped at lower flow rate due to soap formation in the feed tank. The results showed that the optimal condition of methanolysis was found at a methanol to oil molar ratio of 5:1 and a flow rate of 30 ml/min which resulted in maximum yield of 93%. This flow rate was corresponding to residence time of 1.33 min which is much faster than the reaction time needed in a batch reactor to achieve similar yield. FTIR analysis showed that the product formed is biodiesel. It is characterized by the formation of absorption at a wave number of 1435 cm^{-1} , which is evidence of the formation of methyl ester groups. The final biodiesel met EN 14214 and SNI standards. It shows a promising feature of flow type microwave reactor to produce biodiesel.

Key words: palm oil, methanolysis, biodiesel, microwave, flow reactor.

Introduction

Biodiesel offers many benefits as an alternative energy resource including being derived from a renewable domestic resource, thereby reducing the dependence on petro-diesel, and being biodegradable and non-toxic nature (Datta and Mandal, 2016). The total annual petroleum demand in the world increased from 90.3 in 2012 to 120.9 (million barrels per day) in 2040 with an average annual increase of 1.0% between 2012 and 2040 (USEI Administration, 2016). Further, petroleum fuel combustion has been known as the main reason for climate change and global warming. Annual production of CO₂ emissions has increased significantly in recent years. According to projected data, world energy-related CO₂ emissions rise from 32.2 billion metric tons in 2012 to 35.6 billion metric tons in 2020 and to 43.2 billion metric tons in 2040 (USEI Administration, 2016). Therefore, the demanding needs for a clean-burning and sustainable fuel such as biodiesel is constantly growing to avoid future problem of energy supply.

In a typical method of biodiesel preparation, reaction between a plant based oil with an alcohol in the presence of a homogeneous catalyst takes place under conventional heating; heat is transferred to the reaction molecules through convection, conduction, and radiation from the surface of the reactor. Microwave irradiation has become a prospective energy source for many organic syntheses, wherein chemical conversions are accelerated because of selective absorption of microwave energy by polar molecules, non-polar molecules being inert to the microwave dielectric loss (Varma, 2001). Many researches in the recent years show the microwave-assisted synthesis of biodiesel is faster, takes less than 5–6 min, gives higher yields, and produces fewer byproducts (Vyas *et al.*, 2010; Motasemi and Ani, 2012; Marwan and Indarti, 2016). Separation of the glycerol layer is easy and fast (Refaat *et al.*,

2008). Since the mixture of plant based oil, alcohol, and homogeneous base catalyst contains both polar and ionic components, fast heating is observed upon microwave irradiation, and because the energy interacts with the reacting compounds on a molecular level, a very efficient heating can be acquired (Barnard *et al.*, 2007). Microwave heating shows superior performance over conventional methods, where heating can be relatively slow and inefficient due to lack of energy transfer rate by convection currents and the thermal conductivity of the reaction mixture (Koopmans, 2006).

In the present work, preparation of palm oil biodiesel was studied by utilizing a flow reactor and microwave heating. Such flow system is much more suitable for large scale production. The methanolysis was catalyzed by sodium hydroxide and carried out at different flow rates and methanol to oil molar ratios. The resulted biodiesel was characterized for its functional groups, and some physical properties.

Materials and Methods

The refined palm oil was purchased from a local store. The palm oil, methanol 99.8% (Aldrich), sodium hydroxide, and deionized water were used as received. Experiments were performed in a modified Panasonic's NN-ST 342M model microwave unit, working at frequency of 2.45 GHz and maximum power output 800 W. A coiled glass tube (made of Pyrex, 126 cm in length x 0.635 cm in inside diameter) was installed inside the microwave chamber. The reaction fluid was circulated by a peristaltic pump (MasterFlex).

Transesterification was carried out at fixed parameters for the oil amount of 250 g and catalyst loading of 1% (w/w of the oil). Different flow rates (10, 30, 60, and 90 ml/min) and molar ratios of oil and methanol (1:3, 1:4, and 1:5) were selected for the transesterification reactions. Fig. 1 shows arrangement of microwave reactor for the present experiments. The oil, methanol, and the catalyst were charged into a 1.0 L feed flask and stirred during the experiments. The mixture was flowed to the reactor inlet by a peristaltic pump at selected flow rate until the mixture in the feed flask was empty. The reactor outlet was connected to a product flask. During the reaction, the microwave oven was run with heating set at low-micro power. Thereafter, the reaction mixture was cooled to room temperature. The reaction mixture was settled in a separatory funnel overnight, and the biodiesel phase (upper layer) was obtained. Finally, the biodiesel was washed with warm water three times, and dried by adding sodium sulphate. The yield of biodiesel was evaluated by gravimetric method. As a comparison, the palm biodiesel was also prepared by conventional technique in a stirred reactor by water bath heating at 60°C for 15, 30 and 60 min. The agitation speed was kept constant at 200 rpm.

The resulted biodiesel was characterized to determine its density, viscosity, water content, acid number, and refraction index. The chemical changes were identified by Fourier Transform Infrared (FTIR) Spectrophotometer (Model 8400S, Shimadzu) equipped with Interferometer to exclude the effect of moisture and carbon dioxide in the surrounding atmosphere.

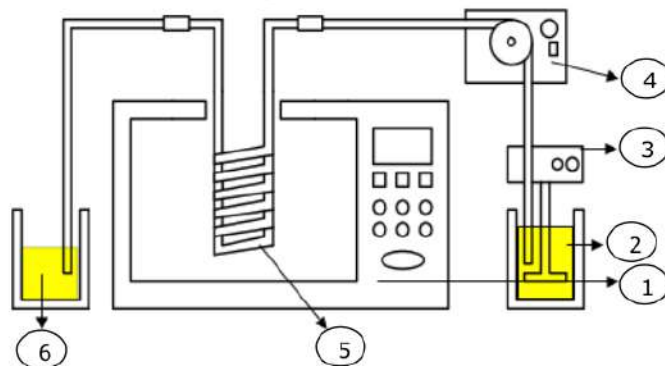


Figure 1. Schematic experimental setup (1. microwave oven, 2. feed flask, 3. stirring unit, 4. peristaltic pump, 5. coiled glass tube, 6. product flask)

Results and Discussion

The reaction mixture was pumped through the coiled glass tube in a single pass. It is essential to determine a precise transesterification time to ensure completion of the reaction. For a flow system, the reaction time corresponds to its residence time, which is determined by the flow rate. Analysis of the

outlet flow indicates that biodiesel was being formed. Fig. 2 shows the biodiesel yield with flow rate for NaOH 1% at different methanol to oil molar ratios. The yield was increased as the flow rate was reduced from 90 ml/min to 30 ml/min, and then the yield was significantly dropped. At flow rate of 10 ml/min, soap formation in the feed tank was observed. It shows that the optimal condition of methanolysis was found at a methanol to oil molar ratio of 5:1 and a flow rate of 30 ml/min which resulted in maximum yield of 93%.

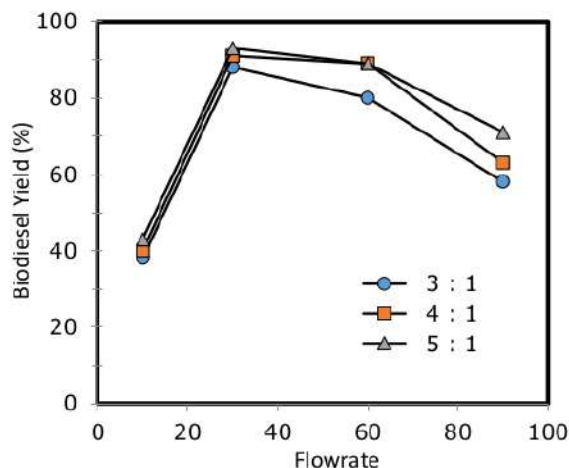


Figure 2. Biodiesel yield at different flow rates and methanol to oil molar ratios.

In the previous work (Marwan *et al.*, 2015), preparation of biodiesel in batch mode microwave reactor resulted in maximum yield of 94-96% for reaction time of 6-10 min, while the conventional heating method gave similar maximum biodiesel yield after 45 min. The maximum yield of 93% in the present work was observed at the flow rate of 30 ml/min. This flow rate was corresponding to residence time of 1.33 min which is much faster than reaction time needed in the batch mode to achieve similar yield. This result is comparable with the residence times of 1.75 min and 2 min found in Choedkiatsakul *et al.* (2015) and Encinar *et al.* (2012), respectively. Higher biodiesel yield at lower flow rate was due to long exposure time to microwave irradiation, and simultaneously causing an increase in thermal gradient during the reaction (Encinar *et al.*, 2012). Thermal microwave effects are revealed being dominant for homogenous-catalyzed reactions (Mazubert *et al.*, 2014).

Theoretical molar ratio of oil to methanol of 1:3 is required for the reaction, but higher than the stoichiometric value is necessary in practical production to enhance the degree of reaction completion. Moreover, effect of the molar ratio may be a key parameter due to high microwave absorption of methanol (Encinar *et al.*, 2012). Owing to its high dielectric constant ($\epsilon = 33$) as compared to palm oil ($\epsilon = 3$), methanol strongly absorbs microwave energy (Choedkiatsakul *et al.*, 2015). In this study, yield of biodiesel reached 88% for the reaction at stoichiometric composition and flow rate of 30 ml/min. Higher yields of 91% and 93% were obtained as the molar ratio was increased to 4:1 and 5:1, respectively. Effect of the molar ratio was more pronounced at higher flow rates or shorter residence times.

Fig. 3 shows FTIR spectra of the obtained biodiesel. Evidence of the formation of ester groups was characterized by a specific absorption band at 1435 cm^{-1} arising from (CO)-O-CH₃. The other strong peaks were related to carbonyl (C=O) at 1737 cm^{-1} and C-O (antisymmetric axial stretching and asymmetric axial stretching) at $1300\text{-}1000\text{ cm}^{-1}$. In addition, the stretching vibrations of CH₃, CH₂, and C-H of the fatty acid chains appear at frequency around 2916 , 2854 , and 2999 cm^{-1} , whereas the bending vibrations (ν_{CH_2}) of these groups appear at $1475\text{-}1350$, $1350\text{-}1150$, and 719 cm^{-1} respectively. These facts are in good agreement with biodiesel spectra reported elsewhere (Naureen *et al.*, 2015; Rabelo *et al.*, 2015; Marwan *et al.*, 2015).

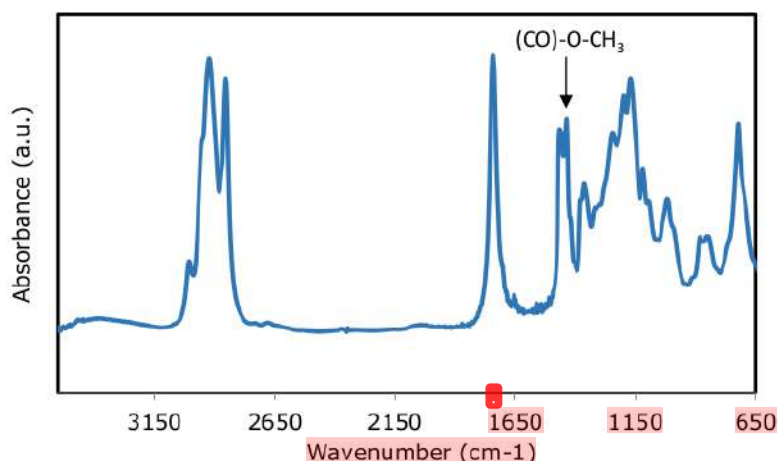


Figure 3. Infra-red spectra of the biodiesel produced in the microwave assisted flow reactor

Quality assessment was performed using physicochemical parameters such as density, viscosity, refraction index, acid number, and water content, and determined according to the EN14015 and ASTM D6751 standard methods. The results are listed in Table 1. The finally obtained biodiesel properties were within the mentioned range of biodiesel fuel standards.

Table 1. Quality assessment of biodiesel produced in the microwave assisted flow reactor

Properties	This Work	EN 14214	SNI
Density at 15°C	896 kg/m ³	860-900 kg/m ³	850-890 kg/m ³
Kinematic Viscosity at 40°C	5,2 mm ² /s	3,5-5,0 mm ² /s	2,3-6 mm ² /s
Refraction Index	1,44	-	1,45
Acid Number	0,07	max 0,5	max 0,8
Water Content	0,012%	-	max 0,05%

Conclusions

A flow reactor system with heating by microwave irradiation was adopted for preparation of biodiesel. Refined palm oil was reacted with methanol, using sodium hydroxide as homogenous catalyst. The most influential variable was flow rate, which corresponds to residence time and also temperature gradient of the reaction. The optimal condition of methanolysis was observed at a methanol to oil molar ratio of 5:1 and a flow rate of 30 ml/min which resulted in maximum yield of 93%. This flow rate was corresponding to residence time of 1.33 min which is much faster than reaction time needed in a batch reactor to achieve similar yield. The study also showed that the quality of the produced biodiesel satisfies the European and Indonesian standards; hence, it can provide an alternative. Moreover, microwave heating offers a fast and easy route to this important biofuel with advantages of enhancing the reaction rate, and lowering production cost that making the biodiesel more economically feasible and being attractive to the consumers.

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