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Transesterification of Palm Oils Catalyzed by Ionic Liquid in Microwave Heated Reactors

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Biodiesel is a renewable, carbon neutral liquid fuel produced from vegetable oils or animal fats with alcohol via catalytic transesterification reaction. Conventionally, alkaline-catalysed transesterification using convective heating takes long time to complete. Alkaline catalysts used are usually non-recyclable, environmentally unfriendly and could react with free fatty acids to form soap. Recently, ionic liquids have been shown to be effective in catalyzing transesterification. Furthermore, microwave irradiation has been shown to boost heat transfer to the reactants, making the reaction time shorter than the conventional heating. In this work, biodiesel production from microwave-irradiated transesterification of palm oils with methanol using a green ionic liquid was investigated. The ionic liquid (ChOH) was synthesized from choline chloride (ChCl) with potassium hydroxide (KOH) and characterized by Fourier transform infrared spectroscopy. The batch experiments were setup and carried out in an 800 W microwave oven with a flask reactor connected to a condenser. The continuous experiments were setup and carried out with a polytetrafluoroethylene (Teflon) tubing connected to a Teflon valve and a pump. Operating condition was oil to methanol ratio (1:15), reaction time (8 min), power of microwave (800 W), and catalyst loading (4 wt%). Methyl ester content was determined by gas chromatography and mass spectrometer.From the findings, it was shown that the ionic liquid was effective in catalysing transesterification of palm oils. Microwave heating proved to accelerate the reaction in short time. The methyl ester content was found to be 87 and 82 % for the batch and continuous experiments. The ester content was quite low, compared to the conventional heating. Further investigation was needed to find high biodiesel yield. The ChOH could also be reused several times but its effectiveness to produce biodiesel may be degraded, in comparison with the fresh catalyst.

1. Introduction

Energy consumption has surged continually after the industrial revolution. Fossil fuel is the main energy source for advancing the world, though pollutions such as sulfur oxides (SO_x), nitrogen oxides (NO_x), and especially carbon oxides (CO_x) are emitted (Simasatitkul and Arpornwichanop, 2019). Many countries issued a policy to reduce carbon emissions (Lee et al., 2018). Adoption of bio-renewable energy is one way to reduce the climate change effect from fossil fuels such as pyrolysis (Prasertpong and Tippayawong, 2019), gasification (Sittisun et al., 2019), and simple chemical conversion (Tippayawong and Chanhom, 2011). Biodiesel is one of the bio-renewable energy sources, which is easy to produce. Feedstock is simple and abundant. Palm oil is the main dominant biodiesel feedstock in South East Asian countries including Indonesia, Malaysia, and Thailand (Silitonga et al., 2013). Palm oil mill effluent is posed an environmental issue. It can solve with microalgal biotechnology (Kamyab et al., 2019). Biodiesel production from palm oil is produced via transesterification by triglycerides, which the main chemical in palm oil, react with alcohol such as methanol or ethanol and catalysts (Ullah et al., 2018), as shown in Figure 1.

In recent years, ionic liquids (ILs) have been accepted as new green chemicals that are capable of revolutionizing chemical processes. ILs are basically organic salts which exist in liquid state at temperature below 100 °C (Soares et al., 2019). ILs consist of cations and anion. Normally, the cations are composed of organic, while anions can be organic or inorganic. They had the chemical interactions between components. The common cations are nitrogen or phosphorous containing compounds (Zhao and Baker, 2013) such as

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alkylammonium, 1,3-dimethylimidazolium and tetramethyl phosphonium. The common choices of anions include BF_4^-, Cl^-,and $CH_3CO_2^-$. Many ILs are proven to be poorly biodegradable and relatively toxic. A new interesting IL is called deep eutectic solvents (DES). It is formed from the mixture of organic halide salts with hydrogen bond donor to a complex organic agent. They can form eutectic mixtures, which are in liquid state at temperatures below 100 °C. DESs have some advantages over ILs, such as easy preparation, high purity, low cost, no reactivity with water, non-toxicity and biodegradability (Chen and Mu, 2019). The deep eutectic ILs became a target of studying biodiesel production. Choline chloride (ChCl) is one of the interesting deep eutectic ILs, which can be developed to catalyze for biodiesel synthesis. The choline is not expensive and biodegradable. Fan el at. (2013) studied biodiesel production via transesterification using choline ionic liquid compound as a catalyst. The result showed that choline hydroxide (ChOH) was best for biodiesel production with conventional heating. It needs long reaction time to be synthesized.

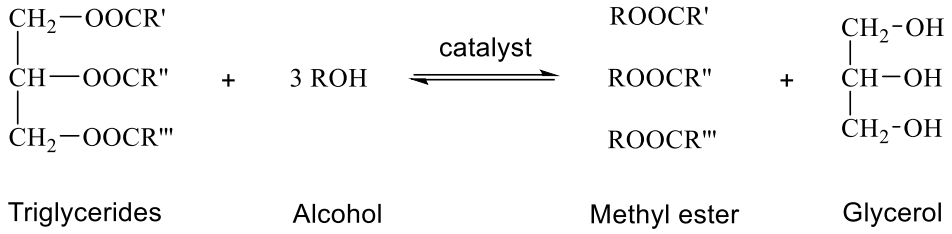

Figure 1: Biodiesel production via transesterification

Microwave is an alternative heating method for reducing the reaction time because microwave irradiation delivers the energy directly to the target. The transfer of heat is more effective than the conventional heating (Motasemi and Ani, 2012). Lin et al. (2013) investigated the use of the 4-allyl-4-methylmorpholin-4-ium bromine ([MorMeA][Br]) ionic liquid as a catalyst in a batch process. It was shown that maximum biodiesel yield of 89 % could be achieved with a reaction time of 6 min. The catalyst can be reused for seven times repeatedly. Tippayawong et al. (2012) improved microwave irradiation technique by adopting a flow reactor. The improved microwave was used in biodiesel production using jatropha oil, methanol and sodium methoxide ($NaOCH_3$) as a catalyst. Results showed that jatropha oil can be converted to biodiesel with a yield of 97 % within 0.5 min.

It was notable that reported works on the combined use of ionic liquids and microwave irradiation were relatively rare for transesterification of vegetable oils. From the existing literature, no report was found for ionic liquid catalyzed and microwave heated reaction in a continuous flow reactor.

The objective of this study was to investigate ChOH ionic liquid catalyst for transesterification in batch and continuous microwave heating processes. Palm oil was used as a representative vegetable oil. To the authors' knowledge, this was the first time that ChOH ionic liquid was investigated in a microwave heated, continuous flow reactor.

2. Material and methods

2.1 Materials

Palm oil was purchased by Morakot Industries plc.in Bangkok. Methanol (AR, 99.9 %), and n-Hexane (AR, 95 %) were bought from RCI Labscan. Choline chloride (≥ 98 %), potassium hydroxide (≥ 85 %) and 1-butanol (99.9 %) were purchased from Sigma-Aldrich. The standard heptadecanoic acid-methyl ester was obtained from Dr. Ehrenstorfer GmbH (99.3 %).

2.2 Ionic liquid preparation and analysis

Choline hydroxide (ChOH) was synthesized from equimolar choline chloride and potassium hydroxide in methanol, shown in Figure 2.

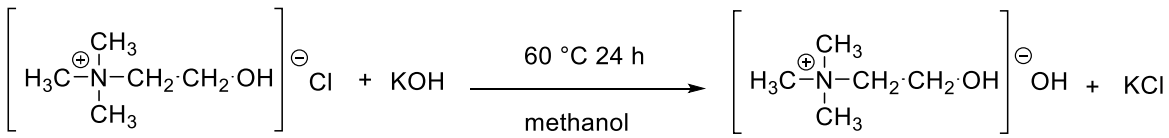

Figure 2: *Synthesis of choline hydroxide using choline chloride and potassium hydroxide*

The solution was subjected to stirring at 60 °C for 24 h (Fan el at., 2013). Thereafter, it was cooled to room temperature and potassium chloride was removed by filtration. The excess methanol was evaporated away from the mixture to obtain the ChOH ionic liquid catalyst. Basicity of the ionic liquid in methanol solution was determined by a pH meter and Fourier transform infrared spectroscopy (FT-IR). The liquid film was used for recording FT-IR of ChOH on a FT-IR spectrophotometer in the 4,000 – 400 cm^{-1} scanning ranges.

2.3 Experimental set-up and procedure

2.3.1 Batch reactor

The batch experiments were carried out in a 250 mL single neck reaction flask containing palm oil, methanol, ChOH catalyst and boiling chips. The microwave reactor has a maximum power of 800 W. The flask reactor was connected to a reflux condenser in order to condense vaporized methanol. The experimental setup is shown in Figure 3. Initially the experimental mixture of about 100 mL was loaded into the flask. After the reaction, it was placed at room temperature. The reaction products were separated using a funnel, then the upper layer containing mainly methyl esters was collected to be purified by washing three times with water at 50 °C. Impurities, such as residue catalyst, glycerol and excess methanol were removed. Finally, water was removed by heating at 150°C (de Almeida et al., 2015). The lower layer was glycerol and the ionic liquid.

2.3.2 Continuous flow reactor

The continuous flow reactor consists of a tank mounted with a magnetic stirrer, placed in an 800 W microwave oven. The tube reactor was made from a poly-tetrafluoroethylene (Teflon) tubing of 3 mm ID, coiled into the centre of the microwave and connected to the Teflon valve, the tank and a pump, also shown in Figure 3. The mixture, around 100 mL of palm oil, methanol and ChOH, was loaded into the tank. The flow rate was controlled by the valve and the pump. The biodiesel was purified in the same way as the batch experiment.

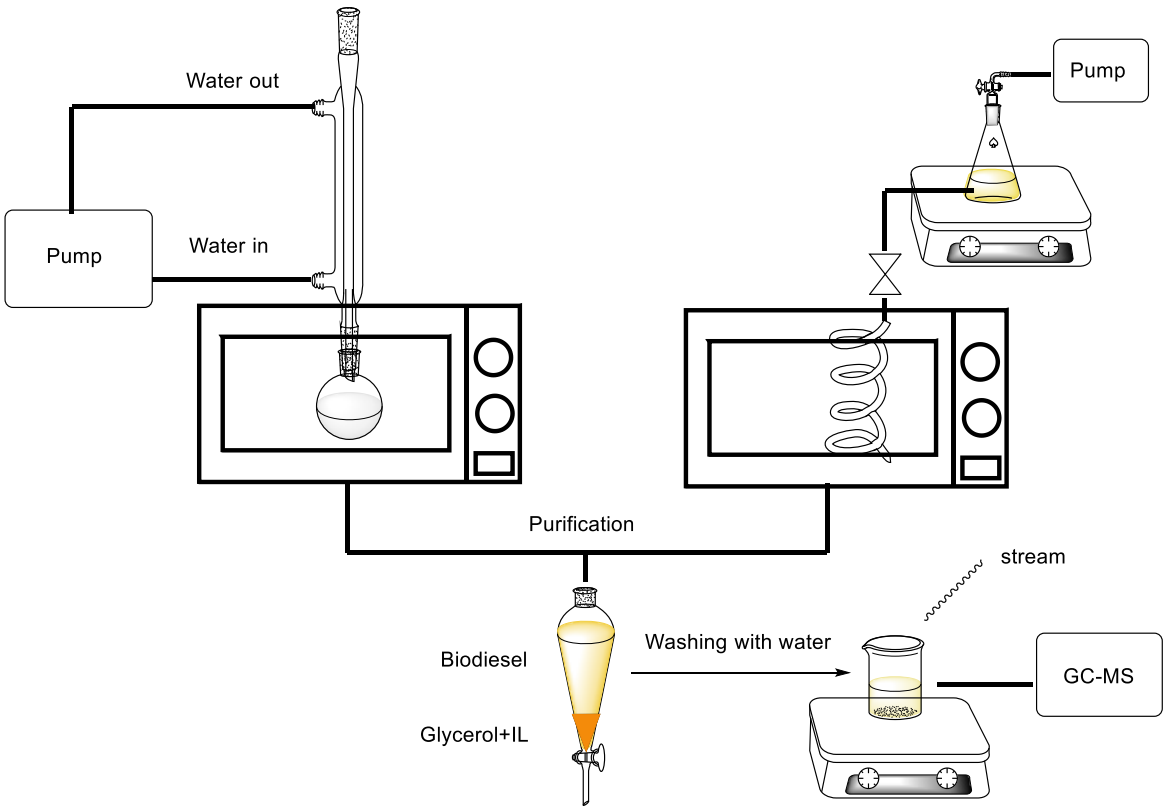

Figure 3: *Overview of the batch and continuous biodiesel production experiments*

2.4 Biodiesel analysis

For biodiesel analysis, the fatty acid methyl ester content was determined by GC/MS equipped with HP-5MS capillary column (30 m×0.25 mm×0.25 μm). The heptadecanoic acid methyl ester (C17:0) was used an

internal standard. The operating condition for the gas chromatography measurements was inlet temperature 230 °C; oven temperature programmed from 45 °C hold for 2 min, 45 – 100 °C at 25 °C/min hold for 10 min, 100 – 190 °C at 5 °C/min hold for 10 min, 190 – 220 °C at 5 °C/min hold for 1 min, 220 – 250 °C at 10 °C/min hold for 5 min,; injection volume 2 µL; 1.5 mL/min helium gas; The condition and the detector were similar to Zhang et al.(2017).The methyl ester content was calculated from the following equation;

$$C_{ester} = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m_{oil}} \times 100\ \% \quad (1)$$

where C: total fatty acid methyl ester content (%); ΣA: sum of the peak area of fatty acid methyl ester from C_{14} to C_{24}:1; A_{EI}: the peak area of the internal standard, palmitic acid methyl ester; C_{EI}: concentration of palmitic acid methyl ester (mg/mL); V_{EI}: volume of palmitic acid methyl ester (mL); m: mass of input biodiesel (mg).

3. Results and discussion

3.1 Characteristic of the ionic liquid

The ChOH obtained was a light orange liquid. The pH value in the methanol solution was more than 14. The IR spectrum can be seen in Figure 4. The pattern observed was similar to those reported by Fan et al. (2013) and De et al. (2011). From the IR spectrum, the featured bands for organic group were shown, in which the O–H stretching was at 3,500 – 3,400 cm^{-1}. Meanwhile, 3,032, 2,976, and 2,848 cm^{-1} represented the C–H stretching of alkane. The C–H bending of CH_2 and CH_3 were at 1,484 and 1,364 cm^{-1}. The C–N stretching was shown at 1,299 cm^{-1} and the C–O stretching was at 1,088 cm^{-1}.

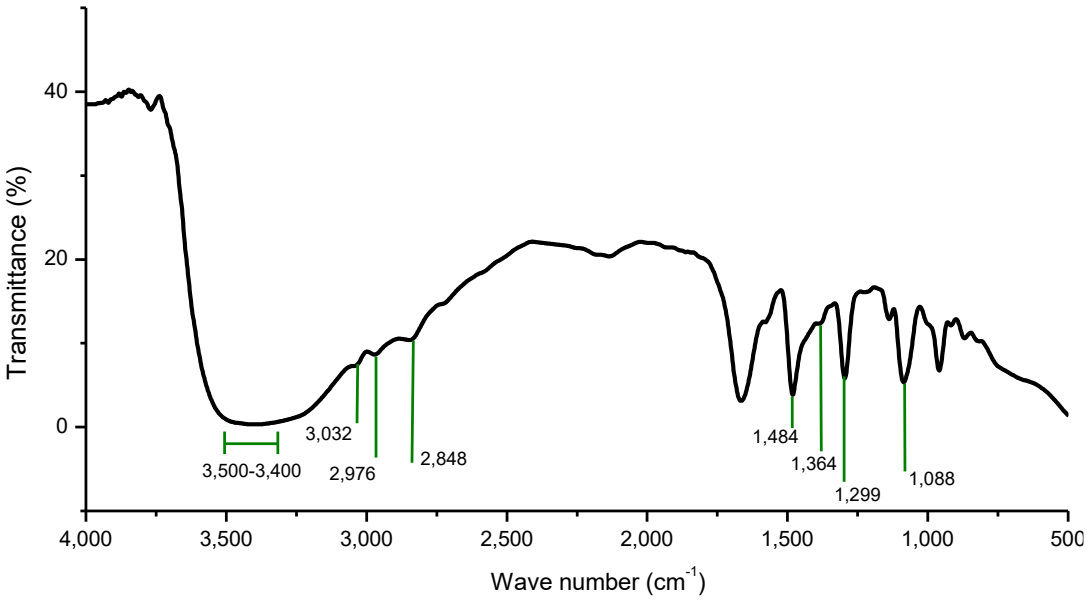

Figure 4: *IR spectrum of ChOH in methanol*

3.2 Biodiesel yield

In this work, the ChOH catalyst was used in two different microwave heated processes, batch and continuous flow reactors. Even though they were at the same condition, the methyl ester content obtained were different. The microwave heated batch experiment gave 87 %, while the microwave heated continuous flow reactor gave 82 % of biodiesel yield. The batch reactor appeared to give better yield than the continuous one because it had the condenser enabling the methanol vapor phase to condense into liquid phase and return to the mixture again. The batch process also had boiling chips for diffusing heat and harmonizing the oil and methanol. Even through the continuous flow setup produced less ester content than the batch process by only 5 %, the batch reactor took longer time to set up and run for a single experiment. The continuous process was more convenient.

The comparative study on the catalytic activities of different catalysts and different operating processes is shown in Table 1. Abdullah et al. (2017) and Tippayawong and Sittisun (2012) reported biodiesel production

from the conventional heating and the continuous microwave heating. The result shows that the methyl ester contents were similar, while the microwave heated continuous flow process was faster. The catalysts in both reports could not be reused. The ChOH catalyst was used for biodiesel production with the conventional heating by Fan et al. (2013). It was shown that high methyl ester content of 96 % could be obtained with no soap formation and IL was reusable. In this work, the continuous process gave lower ester content than that from Fan et al. (2013). But only a single condition was considered. It is interesting to further investigate the continuous process by response surface methodology (Suwannapa and Tippayawong, 2017) combined with Box-Behnken experimental design (Ding et al., 2018). The interesting variables may be the oil to methanol ratio, flow rate, microwave power and catalyst loading, which affect the yields and properties of biodiesel production. These variables were considered by Encinar et al. (2012) and Choedkiatsaku et al. (2015). The optimum condition is expected to give high ester content.

Recycling of ChOH catalyst is also of great interest in this investigation. For the conventional heating, the ChOH catalyst can be reused four times, while all the methyl ester contents obtained were above 80 %. From this work, it was observed that the lower layer volume of the continuous process was less than that from the batch process, affecting the amount of ChOH catalyst recovery. The quality and quantity of the desired ChOH catalyst may be different from the conventional heating process.

Table 1: *Comparison catalyst and process for biodiesel production*

References	Operation	Reaction time (min)	Ester content (%)	Reusability
Abdullah et al.	Conventional heating, palm oil/methanol molar ratio of 1:20, KOH 1.5 wt%, 60°C	60	93	No
Tippayawong et al.	Microwave heated continuous flow reactor, jatropha oil/methanol molar ratio of 1:6 , NaOCH3 1.0 wt%, microwave power 800 W	0.5	96	No
Fan et al.	Conventional heating, soybean oil/ methanol molar ratio of 1:9, ChOH 4 wt%, 60°C	150	97	Yes
This work	Microwave heated batch, palm oil/ methanol molar microwave-assisted ratio of 1:15, ChOH 4 wt%, microwave power 800 W	8	87	Yes
This work	Microwave heated continuous flow reactor, palm oil/methanol molar ratio of 1:15 , ChOH 4 wt%, microwave power 800 W	8	82	Yes

4. Conclusions

The ChOH catalyst proved to be effective in biodiesel production via both batch and continuous reactors with microwave heating. The methyl ester content of 87 % and 82 % were produced. Both processes spent only 8 min for production, faster than the conventional heating. The microwave heated continuous process gave a bit less ester content than the microwave batch process. But, it was faster for all processes considered. Nonetheless, the ChOH catalyst should be investigated further about optimization of methyl ester content and recycling of the catalyst. Further analysis of the ChOH catalyst may include pH measurement and characterization by nuclear magnetic resonance (NMR), since the pH meter may indicate the hydroxyl groups in ChOH catalyst abd the NMR can give the structure of the ChOH catalyst.

Acknowledgments

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