Production of Fatty Acid Methyl Ester from Low Grade Palm Oil Using Eutectic Solvent Based on Benzyltrimethylammonium Chloride

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Abstract. In this study, high content of free fatty acid (FFA) from low grade palm oil (LGPO) was treated using deep eutectic solvent (DES). This DES was prepared via mixing of \( p \)-toluenesulfonic acid monohydrate (PTSA) with benzyltrimethylammonium chloride (BAC). Various effect of reaction conditions were studied such as catalyst dosage (0.5\% to 4.5\%), molar ratio (2:1 to 12:1), reaction time (10 to 120 min) and reaction temperature (30 °C to 80 °C). This study exhibited that 2\% catalyst dosage, 10:1 molar ratio of methanol to oil, 30 min of reaction time and reaction temperature of 60 °C were the optimum condition to reduce the FFA content to less than 2\%.

1. Introduction
Numerous studies were motivated by a demand for renewable source of energy and fluctuating prices of petrol diesel in the current market [1,2]. A mixture of acidic crude palm oil (ACPO) and sludge palm oil (SPO) showed excellent result in producing biodiesel [3]. The low grade oil mixture was the waste oil rejected from palm oil refineries due to its high free fatty acid value of over 5\% [3]. It is a perfect candidate for biodiesel production due to its low cost and it is available domestically.

Deep eutectic solvent (DES) can be used for the treatment of free fatty acid (FFA) and for biodiesel production [3]. DES is a eutectic mixture which can easily synthesize from combination of either salt, salt, hydrogen bond donor (HBD): HBD, and salt: HBD [4,5]. An ammonium based deep eutectic solvent; N,N-diethylenethanol ammonium chloride with \( p \)-toluenesulfonic acid monohydrate (PTSA) was applied as a novel recyclable catalyst [3]. PTSA was mixed with allyltriphenylphosphonium bromide as a phosphonium-based deep eutectic solvent in previous study and also shown a great impact on recyclability study where it can be used up to four runs [6].

Another type of salt benzyltrimethylammonium chloride (BAC) was proposed in this study to prepare novel recyclable DES. This research work presents the catalytic activities of BAC-DES catalyst; BAC mixed with PTSA in esterification of low grade palm oil (LGPO). The optimum condition of the esterification reaction is proposed. The parameters are to be the parameters studied are dosage of catalyst, reaction temperature and time and molar ratio. A multi-unit reactor with reflux condenser using feedback controlled system was used to conduct the experiment.
2. Experimental

2.1. Materials and Method
Low grade palm oil (LGPO) with FFA content of 9.2% was collected from a local palm oil mill, Malaysia. Methanol, potassium hydroxide, benzyltrimethylammonium chloride, p-toluenesulfonic acid monohydrate were purchased from Sigma Aldrich.

2.2. Synthesized of DES based catalyst
The BAC-DES catalyst was prepared using method of Hayyan et al. [3]. The molar ratio of BAC to PTSA was 1:3. The required amount of BAC powder was mixed with PTSA gradually until it becomes a clear homogenous solution. The mixing condition is at 60 °C and the magnetic stirrer was set at 350 rpm using hot plate and magnetic stirrer. The mixture was sealed and placed in desiccator with silica gel to prevent absorption of moisture.

2.3. Synthesized of FAME from LGPO
LGPO was pre-heated at 80 °C before esterification. The required amount of oil sample was placed in multi-unit reactor with reflux condenser and speed controller using feedback controlled system. The specific dosage of BAC-DES catalyst was mixed with methanol until homogeneous prior addition to multi-unit reactor. Esterification was carried out with different catalyst dosage (0.5% to 4.5%, based on oil weight), molar ratio of methanol to oil (2:1 to 12:1), reaction time (10 to 120 min) and various reaction temperature (30 °C to 80 °C). The standard batch was run with 30 g of oil, 12 g of methanol and 0.3 g of catalyst placed in the jacketed vessel. The reaction conditions were at 60 °C, 30 min, and under stirring at 350 rpm. After esterification, the solvent and catalyst was separated using centrifugation. After separation, treated oil was further heated at 75°C in oven to remove excess methanol. The reusability of BAC based DES catalyst was investigated using selected optimum condition and was run without addition of fresh catalyst. The FFA content was evaluated using titration according to AOCS official method Ca 5a-4 [14]. The transesterification of treated oil was fixed as follows: 1% of KOH solubilize in methanol (10:1 molar ratio of methanol to oil) at 60 °C, 30 min, and 350 rpm stirring speed [10].

3. Results and discussion

3.1. Effect of BAC-DES catalyst and molar ratio
This is the first time for BAC based DES to be used for esterification of LGPO to produce biodiesel. BAC is an off-white quaternary ammonium compound with a structural resemblance to acetylcholine [7]. As mentioned above, the targeted FFA after esterification in this study was to be at ≤ 2%. From Figure 1, the reduction of FFA was proportional with increasing dosage of catalyst. The result shows that BAC based DES possessed high catalytic activity. Dosage of catalyst at value 1.5% is sufficient to reduce the FFA content from 9.2% to 1.8% and gives 88.5% FAME conversion. Though it used higher amount compared to other studies, 2% is still considered acceptable dosage to be applied in esterification at industrial scale. Thus, 2% of BAC based DES was selected as the optimum dosage in esterification of LGPO. From figure 1, the conversion of FFA to FAME was found to increase with increasing of dosage used.

Molar ratio was varied from 2:1 to 12: of methanol to oil. From Figure 2, 6:1 molar ratio was sufficient to reduce the FFA content to ≤ 2%. There was no enhancement in the reduction of FFA content after molar ratio 10:1. Thus, 10:1 was selected as the optimum molar ratio to esterify LGPO with the reduction of FFA content from 9.2% to 1.06%. This study slightly advantage compared to other study done by Corro et al where 12:1 molar ratio of methanol was used to esterify Jatropha curcas crude oil with the aid of heterogeneous catalyst [8].
Figure 1. Effect of BAC based DES dosage on the yield of treated LGCPO and the correspondence reduction of FFA content at 30 min reaction time, 10:1 molar ratio, 60 °C, and 300 rpm.

Figure 2. Effect of molar ratio on the yield of treated LGPO and the correspondence reduction of FFA content at 30 min reaction time, 60 °C, 1.5% catalyst dosage and 300 rpm.

3.2. Effect of reaction time and reaction temperature
As shown in Figure 3, the reduction of FFA to targeted limit was achieved even only with 10 min reaction time. It revealed that BAC based DES possessed strong catalytic activity and was able to react with reactant in short period during esterification. Although prolonged the reaction time could lower the FFA content from 9.2% to 0.39%. A period of 30 min was deemed as the optimum reaction time since it reduced the FFA content to 1.61%. A short period of time is preferred to save operating cost of biodiesel production [9,10].
From Figure 4, reaction temperature of 70 °C showed the highest reduction of the FFA content from 9.2% to 1%. However, 60 °C was chosen as the optimum reaction temperature to reduce energy consumption and for economic feasibility. At that temperature, it reduced FFA up to 1.3% which lower than industrial limit [6]. The reaction temperature selected for this study is below the boiling point of the methanol, 64.7°C. As can be seen from Figure 4, the FFA reduction was increased at 80°C and reduced the conversion of FAME to 86.25%. Too high reaction temperature may cause the reaction yield to decrease. The amount of loss is believed to be caused by the vaporization of methanol during reaction [11].

![Figure 3](image3.png)

**Figure 3.** Effect of reaction time on the yield of treated LGCPO and the correspondence reduction of FFA content at 10:1 molar ratio, 60 °C, 1.5% catalyst dosage and 300 rpm

![Figure 4](image4.png)

**Figure 4.** Effect of reaction temperature on the yield of treated LGCPO and the correspondence reduction of FFA content at 10:1 molar ratio, 30 min reaction time, 1.5% catalyst dosage and 300 rpm
3.3. Validity of optimized condition and recyclability

In the present study, 2% of catalyst dosage, 10:1 molar ratio of methanol to oil, 30 min of reaction time and reaction temperature of 60 °C was selected as the optimum operating condition for esterification of LGPO, using BAC-based DES. The optimum condition was able to reduce the FFA content from 9.2% to 1.23%. The 6 consecutive runs were conducted without adding fresh catalyst. According to Figure 5, the percent of reduction of FFA decreased to 50% in the 2nd run, and constantly showed 50% reduction of FFA.

![Figure 5. Recyclability study using BAC-DES catalyst in optimum reaction condition](image)

4. Conclusions

In this study, BAC-based DES was used for the treatment of FFA content in LGPO. It proved to have high catalytic activity as of homogeneous acid catalyst. It has lower cost and easy to prepare in comparison to ionic liquids. This study exhibited that 2% catalyst dosage, 10:1 molar ratio of methanol to oil, 30 min of reaction time and reaction temperature of 60°C were the optimum condition as it gives high FAME conversion.

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