SYNTHESIS OF NOVEL EUTECTIC CATALYST FOR THE ESTERIFICATION OF CRUDE PALM OIL MIXED WITH SLUDGE PALM OIL

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ABSTRACT

In this study, a new eutectic solvent (ES) was synthesised for the first time via mixing (1R)-(-)-camphor-10-sulphonic acid (10-CSA) with choline chloride (ChCl). Camphor-10-sulphonic acid choline chloride eutectic solvent (CSA-ChCl-ES) was used as a catalyst in the esterification reaction of an oil mixture consisting of acidic crude palm oil and sludge palm oil in order to reduce the free fatty acid (FFA) content to less than 2%. The optimal reaction conditions were as follows: 2.5 wt% of catalyst dosage, 10:1 molar ratio, 60°C of reaction temperature and 40 min of reaction time. This study revealed that the novel eutectic solvent possessed high catalytic activity and recyclability, hence highlighting its high potential for biodiesel production.

Keywords: acidic crude palm oil, choline chloride, (1R)-(-)-camphor-10-sulphonic acid, deep eutectic solvent, esterification, free fatty acid, sludge palm oil.

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INTRODUCTION

The scarcity of non-renewable fossil fuels, the fluctuating fuel prices and the growing concern over the threat of global warming, have increased the demand for alternative sources of fuels (Salvi and Panwar, 2012; Silva *et al.*, 2010). To date, the most widespread alternative fuels are based on biodiesel. Biodiesels are mono-alkyl long chain fatty acids esters obtained from the transesterification of fatty acids such as animal fats or vegetable oils (Nieves-Soto *et al.*, 2012).

Crude palm oil (CPO) has been widely used as feedstock for biodiesel production (Elsheikh *et al.*, 2011; Ho *et al.*, 2014). Sludge palm oil (SPO) and acidic crude palm oil (ACPO) were also reported as potential industrial raw material for biodiesel production (Hayyan *et al.*, 2013a; 2014a). However, the high free fatty acid (FFA) content in such low-grade oils and fats is the main obstacle to produce biodiesel using standard alkaline catalyst, as it reduces the yield of biodiesel and conversion rate. Low yields and conversion rates are the results of side reactions such as saponification, which divert the separation process of glycerol from crude biodiesel (Canakci and Gerpen, 2001). Therefore, an esterification reaction with acid catalysts is often required to convert FFA to fatty acid methyl ester (FAME) before the alkaline transesterification reaction (Canakci, 2007; Silva *et al.*, 2010). The common acid catalyst for esterification reaction in industry is sulphuric acid and *p*-toluenesulfonic acid monohydrate (PTSA) (Hayyan *et al.*, 2010a; Canakci and Gerpen, 2001). Recently, (1R)-(-)-camphor-10-sulphonic acid (10-CSA) was introduced as a solid organic catalyst for the treatment of FFA as it

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showed high catalytic activity (Hayyan *et al.*, 2014a). The 10-CSA has also reportedly shown outstanding catalytic activity during the FFA reduction and conversion of FFA to FAME. As a weak organic acid, 10-CSA has promising industrial applications. However, it also possesses significant hygroscopic character, which might impede its applications for the industrial-scale biodiesel production (Hayyan *et al.*, 2014a).

An alternative to this conundrum might entail the conversion of hygroscopic acids to eutectic solvents as noted by Hayyan *et al.* (2013b, c; 2014b). Sulphonic acid-based eutectic solvents are relatively more stable compared to conventional sulphonic acids (Hayyan *et al.*, 2014c). Eutectic solvents or deep eutectic solvents (DES) have recently garnered considerable interest due to their potential as environmental-friendly and compatible solvents (Smith *et al.*, 2014; Alhassan *et al.*, 2015). The application of eutectic solvent (ES) in various industrial processes has been reported, *e.g.* electrochemical energy for the storage device (Bahadori *et al.*, 2015), synthesis of aromatic compound from nucleophilic reagent (Liu *et al.*, 2015), substrate in the enzymatic esterification of selective oleic acid (Zeng *et al.*, 2015) and reaction medium for the synthesis of novel organic synthesis of oxazoles for pharmaceutical purposes (Singh *et al.*, 2013). ES are biodegradable solvents and they exhibit low toxicity compared to conventional ionic liquids and organic solvents (Hayyan *et al.*, 2013b; Juneidi *et al.*, 2015). ES are generally prepared using hydrogen bond donors (HBD) such as sugars, polyols, and carboxylic acids, and simply blended with a hydrogen bond acceptors (HBA) such as choline chloride (ChCl) (Zhang *et al.*, 2012). The infusion of an HBD with the anionic species of an HBA induces a huge depression in the melting point characteristic of the new mixture (Durand *et al.*, 2012). In light the above, the aim of this study was to investigate the functionality of a eutectic solvent comprising 10-CSA and ChCl for the esterification of FFA content.

MATERIALS AND METHOD

Raw Material and Chemicals

CPO and SPO were collected from local mills at Carey Island, Selangor, Malaysia. Methanol, (1R)-(-)-camphor-10-sulphonic acid (10-CSA) and ChCl were purchased from Merck Sdn Bhd, Malaysia with purity of $\geq 99\%$.

Methodology

CPO was mixed with SPO to prepare ACPO with 8.1% FFA content. The FFA limit for this study was fixed at 2%. Jacketed reactor with reflux

condenser controlled by a feedback system was used for the treatment of FFA content where the pre-heated oil (at 70°C for 1 hr) samples were esterified using methanol in the presence of CSA-ChCl-ES as a catalyst. This method was adopted from previous work by Hayyan *et al.* (2013b; 2014c).

The ES was prepared by mixing the ChCl with 10-CSA at a mass ratio of 1:1 for 3 hr at 80°C in a moisture controlled environment (Figure 1). The CSA-ChCl-ES was sealed and kept in vial before use. The CSA-ChCl-ES was mixed with the methanol and then poured in the reactor with the pre-heated oil. CSA-ChCl-ES was used at different dosages and other parameters such as the reaction time, molar ratio, and reaction temperature were optimised.

Figure 1. Preparation of CSA-ChCl-ES.

In the recyclability test, the catalyst dissolved in methanol then the mixture was separated from the treated oils after the esterification reaction using centrifugation and continuously used for the next batch of fresh ACPO sample. The FFA content after the esterification reaction was determined according to AOCS Official Method Ca 5a-4 (AOCS, 1997). The amount of active catalyst used in the reaction was calculated using a catalyst consumption (C.C) Equation (1). C.C is defined as the mass of catalyst consumed per mass of synthesised product (Hayyan *et al.*, 2010b).

$$C.C = \frac{M_{cat}}{M_p} \quad \text{Equation (1)}$$

where:

C.C - catalyst consumption.

M_{cat} - mass of catalyst used to give the synthesised mass of product biodiesel (mg).

M_p - mass of synthesised product biodiesel (g).

RESULT AND DISCUSSION

Effect of 10-CSA-ChCl-ES at Different Dosages

Figure 2 shows the effect of CSA-ChCl-ES on FFA content reduction at different dosages. CSA-ChCl-

Figure 2. Effect of dosage of CSA-ChCl-ES on free fatty acid (FFA) content.

ES possess high catalytic activity, decreasing the FFA content from 8.1% to 1.71% and subsequently 1.2%, while using only 2.5 wt% and 3 wt% of eutectic solvent to oil respectively. The reaction time was fixed at 30 min for all runs hence, the FFA reduction occurred in a short period of a time. Figure 2 also shows that using a catalyst dosage of 2.5%, the FFA was reduced to 1.71% while the conversion rate was 90%. The 3.5 wt% of CSA-ChCl-ES to ACPO was sufficient to reduce the FFA content to 1%. It was reported by Hayyan *et al.* (2014a) that the best catalyst dosage is the minimum dosage that is sufficient to reduce the FFA content rapidly during the course of the esterification reaction. Therefore, 2.5 wt% was selected as the optimum catalyst dosage. Based on the catalyst consumption (CC) of CSA-ChCl-ES in Table 1 and the conversion rate of FFA to FAME, the yield of treated oil was proportional to the amount of the catalyst used. Table 1 showed that 2.5 wt% of dosage, 25.91 mg was needed to produce 1 g of treated oil. In recent study, Hayyan *et al.* (2014a) used 10-CSA while the current study used ChCl as salt and 10-CSA as HBD

to prepare ES. The result showed that the acid did not lose its catalytic activity when converted to ES. CSA-ChCl-ES as an organic catalyst showed slightly low catalytic activity compared to ammonium and phosphonium-based DES (Hayyan *et al.*, 2013c; 2014c).

Effect of Reaction Time

In order to complete the esterification, an adequate reaction time is required. Reaction time for this study was evaluated from 10-120 min as shown in Figure 3. The FFA level was reduced simultaneously with increasing reaction time and the reduction of FFA occurred quickly at 10 and 20 min with 2.16% and 2.02 wt% respectively. The rate of conversion increased with reaction time. Both 30 and 40 min were sufficient to reduce the FFA content. However, 40 min was chosen as the optimum reaction time. This optimum reaction time is acceptable in industrial scale and considered as suitable reaction time for the esterification reaction.

Effect of Reaction Temperature

Thermodynamically, methanol and triglyceride are unable to react at room temperature and atmospheric pressure. This is due to the low solubility of methanol in oil (Nieves-Soto *et al.*, 2012). Thus, the temperature is a vital parameter to induce the esterification reaction. Figure 4 shows the effect of temperature on the reduction of FFA. In order to increase the conversion rate of treated oil, optimum temperatures are required for the system to exceed the activation energy of the reaction (Fan *et al.*, 2017). It is evident that increasing the reaction temperature will decrease the FFA level. The slight

TABLE 1. EFFECT OF CSA-ChCl-ES ON YIELD OF TREATED ACIDIC CRUDE PALM OIL AND CATALYST CONSUMPTION

Dosage of catalyst (%)	Yield (%)	Catalyst consumption (mg g ⁻¹)
0.5	90.0	5.55
1.0	91.5	10.93
1.5	96.0	15.63
2.0	96.2	20.79
2.5	96.5	25.91
3.0	96.6	31.06
3.5	97.0	36.08

Figure 3. Effect of reaction time on free fatty acid (FFA) content.

Figure 4. Effect of reaction temperature on free fatty acid (FFA) content.

increment of FFA content at 80°C was not advisable due to methanol evaporation. In addition, the higher temperature required higher energy consumption (Hayyan *et al.*, 2013b). Reaction temperature at 70°C reduces the FFA content from 8.01% to 1.04%. However, in order to save the cost of maintenance and operation, a minimum reaction temperature is highly desirable in esterification reaction (Hayyan *et al.*, 2014b). Thus, a temperature of 60°C was selected as optimum reaction temperature as it was sufficient to reduce the FFA level to 1.88% (which is lower than the limit of FFA required in industry).

Effect of Molar Ratio

In term of solvent choice for the esterification, methanol is more favourable compared to other

alcohols, because of its low viscosity, low cost, short reaction time, low energy requirements and overall better performance (Guerrero-Fajardo *et al.*, 2010). Figure 5 shows the effect of methanol loading for the esterification of FFA content. Results showed that 8:1 can be used for FFA reduction. However, the FFA level was 2% at a molar ratio of 8:1, whereas a molar ratio of 10:1 reduced the FFA content to less than 2%. Figure 5 shows no significant improvement while using methanol loading of more than 10:1. Similar results were also obtained by Suresh *et al.* (2017) as no significant increase of conversion rate was recorded after a molar ratio of 10:1 using 1% of partially sulphonated polystyrene (PSS). Therefore, 10:1 was considered as the optimum molar ratio for the esterification reaction. Ma and Hanna (1999) mentioned that an excess ratio of methanol

is required to maximise the yield of FAME and to drive the reversible reaction towards equilibrium. Moreover, a 10:1 molar ratio is applicable in massive plant as the cost of the production of biodiesel is proportional to the amount of solvent used (Hayyan *et al.*, 2014b).

Validation and Recyclability

The results showed that the optimum conditions necessary to reduce the FFA content below 2% were 60°C temperature, 2.5 wt% dosage of CSA-ChCl-ES to oil, the reaction time of 40 min and 10:1 molar ratio. The reusability and recovery of catalyst will have a significant impact on the economics of the industrial processes. *Figure 6* shows that this catalyst can be recycled for five consecutive runs. The first two recycling runs have the highest FAME

conversion while the third and fourth recycling runs have FAME conversion between 40%-50%. To have two or three continuous recycling runs of the homogenous catalyst can be considered as a good potential for the industrial application of biodiesel production. However, more R&D studies in the field of homogeneous catalysts are highly recommended.

CONCLUSION

The optimal conditions for this study were 2.5 wt% of catalyst dosage, 10:1 molar ratio, 60°C reaction temperature and 40 min reaction time. The agro-industrial feedstocks such as ACPO and SPO were the most effective raw materials for biodiesel production because of their availability and low price. The FFA content of an SPO/CPO mixture was

Figure 5. Effect of molar ratio on free fatty acid (FFA) content.

Figure 6. Recycling of CSA-ChCl-ES.

successfully reduced from 8.1% to below 2%, which is the limit required in industry. The reusability of the catalysts was also acceptable. This work shows that CSA-ChCl-ES is capable of becoming a novel catalyst for the esterification reaction.

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