Application of a Novel Catalyst in the Esterification of Mixed Industrial Palm Oil for Biodiesel Production

Adeeb Hayyan · Mohd Ali Hashim · Maan Hayyan

Abstract Mixed industrial palm oil (MIPO) is proposed in this study as a renewable and agro-industrial raw material to produce biodiesel fuel. MIPO was obtained by mixing of acidic crude palm oil with sludge palm oil. Due to the high level of free fatty acid (FFA) in MIPO (8.5 %), esterification is needed to remove the acidity to the minimum level before biodiesel production. This is the first time 1-propanesulphonic acid (1-PSA) has been introduced as a catalyst for the pretreatment of MIPO. Using optimum conditions, the FFA content was successfully reduced from 8.5 % to less than 1 %. The biodiesel produced meets the international standards (ASTM D6751 and EN 14214). 1-PSA is therefore a promising catalyst that can be used to treat various types of acidic oils.

Keywords 1-Propanesulphonic acid · Biodiesel · Esterification · Free fatty acid · Sludge palm oil · Mixed industrial palm oil

Introduction

Biomass and agricultural residues are available sources for generation of renewable energy to partially substitute petroleum fuels [1, 2]. Biodiesel is a clean, biodegradable, and nontoxic fuel made from biological sources [3, 4]. This biodiesel can be produced by the alkaline transesterification reaction if the free fatty acid (FFA) content is lower than 1–2 %. However, if the oil contains higher FFA content, pretreatment (esterification) is required to remove the FFA content [5]. Currently, the investigation of new renewable raw materials for synthesis of biodiesel is one of the popular areas of research in the biodiesel industry. Availability of low-cost feedstocks is a prerequisite for economic and commercially viable production of biodiesel. Application of industrial low-grade oils for biodiesel production will reduce the overall cost of biodiesel production. Acidic crude palm oil (ACPO) and sludge palm oil (SPO) are generated from palm oil mills [6, 7]. These low-grade oils have great potential as raw materials for biodiesel production. There are many types of common homogenous acids employed for fatty acid methyl ester (FAME) conversion, such as sulfuric acid [8], *p*-toluenesulfonic acid (PTSA) [7, 9], trifluoromethanesulfonic acid [10], ethanesulfonic acid [6], hydrochloric acid [11], chromosulfuric acid [12, 13], methanesulfonic acid [14], and (1R)-(−)-camphor-10-sulfonic acid [15]. Ionic liquids (ILs) were used as a precatalyst for esterification of crude palm oil (CPO) [16]. Recently, phosphonium or ammonium-based deep eutectic solvent was used as recyclable acid catalyst for the treatment of low-grade palm oil [17–19]. The introduction of new types of catalyst for the esterification of mixed acidic oils such as ACPO and SPO can be considered significant. This study proposed 1-propanesulphonic acid (1-PSA) as a potential catalyst for FFA conversion to FAME. A number of operating conditions and recycling studies were conducted and reported.

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Methods and Materials

Raw Materials and Chemicals

MIPO was obtained from a local mill in the state of Selangor in Malaysia. Potassium hydroxide (KOH) pellets (85 %) and methanol (99.8 %) were purchased from R&M Chemicals. 1-Propanesulfonic acid ($C_3H_8O_3S$) (>99 %) was purchased from Sigma-Aldrich.

Biodiesel Preparation

MIPO was obtained by mixing of ACPO oil with SPO. The MIPO was heated to reduce viscosity for ease of handling. The experimental design and procedure of biodiesel production adopted in this study is similar to that reported by Hayyan et al. [6]. Operating conditions were optimized based on the FFA content reduction and conversion of FFA to FAME. A catalyst recyclability study was conducted to examine the catalytic activity of 1-PSA using the optimum operating conditions. The method used to recover the 1-PSA catalyst was by evaporation of methanol followed by centrifugation. Transesterification was then conducted using 1 wt% of KOH to the treated MIPO. The molar ratio (methanol to treated MIPO) was 10:1 and the reaction time was 60 min. The purified biodiesel fuel was characterized using the of biodiesel international standard specifications. The MIPO fatty acid profile was investigated using GC/MS. Measurements of MIPO physical properties were made using test methods published by Malaysian Palm Oil Board (MPOB) [20].

Results and Discussion

MIPO Characterization

The characteristics of MIPO, ACPO, and CPO are presented in Table 1. The results show that MIPO has almost similar physical properties, comparable to that of ACPO. The moisture content of MIPO was slightly higher than ACPO while moisture content of CPO was significantly lower than ACPO and MIPO. Due to the long-time storage, the peroxide value was higher compared to CPO and almost close to ACPO. Table 2, shows the fatty acid profile of MIPO. According to Table 2, the oleic and palmitic acids have the higher concentration in MIPO. The total concentration of saturated fatty acids is slightly higher than total concentration of unsaturated fatty acids.

Table 1 Characterization of ACPO, CPO, and MIPO

Parameters	ACPO [6]	CPO [21]	MIPO
Free fatty acid, FFA (%)	8.6	3.20	8.5
Peroxide value (ml/mol/kg)	7.45	0.70	7.73
Moisture content (%)	1.105	0.18	1.54
Iodine value, IV	56	52.00	56.7
Impurities (%)	0.056	0.03	0.058
Saponification value	197.0	–	192.4
Unsaponification matter (%)	6.70	–	6.50
Ash (%)	0.011	–	0.017
Acid value (mg KOH/mg)	17.20	4.70	18
DOBI (index)	1.80	2.70	1.64
Carotenoids (ppm)	300	-	310

Effect of 1-PSA Dosage, Molar Ratio, Reaction Temperature, and Reaction Time

Figure 1 shows the effect of different dosages of 1-PSA on the reduction of FFA content in MIPO and the FFA conversion to FAME. The targeted content of FFA in this study is 1 %. The dosage of 1-PSA to MIPO ranged from (0.25–2 wt/wt%). According to the results, 1-PSA exhibits a very good catalytic activity in the esterification of MIPO. Low catalyst dosages such as 0.25 and 0.5 wt% of 1-PSA to MIPO give the same reduction of FFA value, i.e., 2 %. Figure 1 shows that 1-PSA reduces the FFA content to less than 1 % at a catalyst dosage of 0.75 wt%. The FFA could be reduced to 0.43 %, and a conversion of about 95 % could be achieved using 2 % catalyst dosage. The optimum catalyst dosage was 0.75 %, at which the FFA was reduced to 0.81 % and the FFA conversion became almost constant.

Alcohols (methanol or ethanol) are the main chemicals used for the esterification reaction. The esterification reaction needs enough loading of methanol to achieve high conversion of FAME [9–11]. The molar ratio of methanol to MIPO was varied from 2:1 to 14:1. Figure 2 presents the molar ratio effect on the reduction of FFA content and FFA conversion to FAME. It was found that the FFA reduced from 8.5 to 5.5 %

Table 2 Fatty acid composition of MIPO

Fatty acids	Structure	Type of fatty acid	Fatty acids (wt%)
Lauric acid	C12:0	Saturated	0.38
Myristic acid	C14:0	Saturated	1.1
Palmitic acid	C16:0	Saturated	44.92
Palmitoleic	C16:1	Unsaturated	0.41
Stearic acid	C18:0	Saturated	3.92
Oleic acid	C18:1	Unsaturated	39.74
Linoleic acid	C18:2	Unsaturated	9.09
Alpha-linolenic acid	C18:3	Unsaturated	0.23
Arachidic acid	C20:0	Saturated	0.34

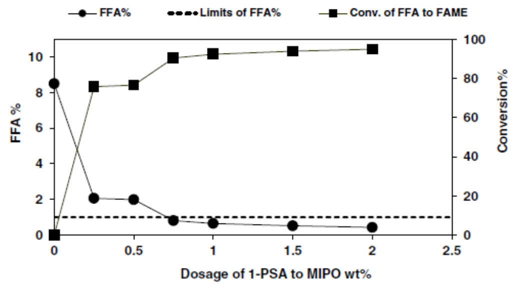

Fig. 1 Effect of 1-PSA dosage on FFA content reduction and FAME conversion at 10:1 molar ratio, 60 °C, and 30-min reaction time

and 3 % using 2:1 and 4:1 methanol to MIPO, respectively. At molar ratio of 6:1, the FFA content was slightly higher than the targeted limit of FFA content. Loading of menthol to MIPO at 8:1 was found to be less than 1 %, and there was no momentous change observed with high loading of methanol (8:1–14:1). Therefore, 8:1 methanol to MIPO was picked out as the optimum molar ratio for esterification of MIPO.

Figure 3 shows the effect of reaction temperature. The results show that the low reduction and conversion of FFA was found at 40 and 50 °C. However, at 60 and 70 °C, it gives high FFA conversion and the FFA content was reduced from 8.5 % to less than 1 %. At high reaction temperatures, i.e., 80 °C, the FFA content was reduced from 8.5 to 1.3 % due to evaporation of methanol during the course of the reaction and consequently will reduce the FFA conversion to FAME. In order to save energy, the reaction temperature is required for the pretreatment process; 60 °C was identified as the optimum for the treatment of MIPO.

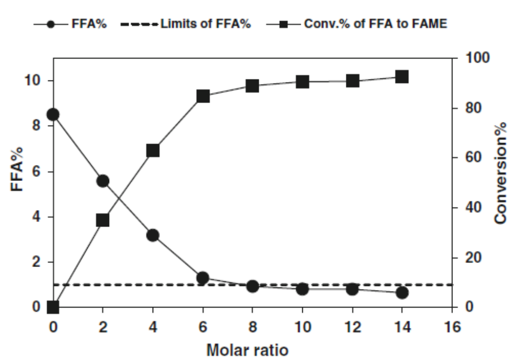

Fig. 2 Effect of molar ratio on FFA content reduction and FAME conversion at 0.75 % of 1-PSA to MIPO, 60 °C, and 30-min reaction time

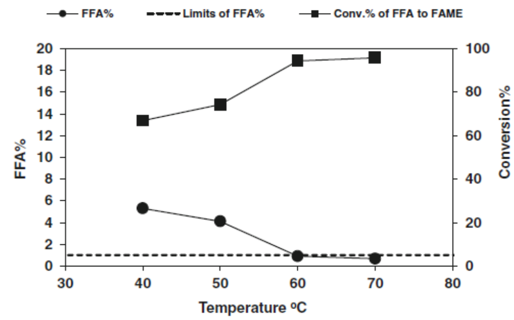

Fig. 3 Effect of reaction temperature on FFA content reduction and FAME conversion at 8:1 molar ratio, 0.75 % of 1-PSA to MIPO, and 30-min reaction time

The reaction time varies within a wide range (10–60 min), as elucidated in Fig. 4. It was found that the rate of conversion and reduction of FFA content was enhanced significantly with an increase in reaction time. After 10–20 min the FFA decreased from 8.5 to 3.9 %, and this is considered a high level of FFA content. Significantly, after 30 to 60 min, the FFA content reduced to less than 1 %. Therefore, 30 min was selected as the best reaction time for the esterification of MIPO. This reaction time is considered a shorter period due to high catalytic activity of 1-PSA.

Validation and Catalyst Recycling Study

The optimum conditions were taken to be 0.75 % dosage of 1-PSA, 8:1 methanol to MIPO, 30 min reaction time, and 60 °C reaction temperature. After validation of the optimum conditions used for the esterification of MIPO, it was found that the FFA content 0.97 % (±0.05) and the conversion was 88.65 %. The optimum conditions using 1-PSA are similar to results reported by Hayyan et al. [18, 22] using *N*,*N*-diethylenethanol ammonium chloride-based deep eutectic solvent and

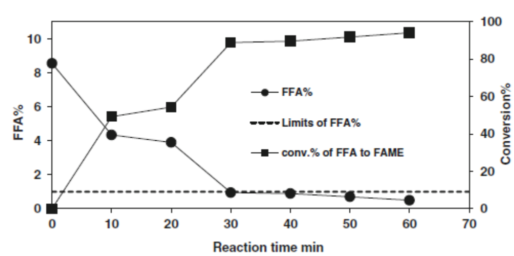

Fig. 4 Effect of reaction time on FFA content reduction and FAME conversion at 8:1 molar ratio, 60 °C, and 0.75 % of 1-PSA to MIPO

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