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Utilization of crude karanj (*Pongamia pinnata*) oil as a potential feedstock for the synthesis of fatty acid methyl esters

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Methyl esters were synthesized from crude karanj oil (CKO) by single step esterification with methanol using sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) as catalysts in a homogeneous batch process. H_3PO_4 was less active than H_2SO_4 during the process as it presented very low ester yields (<20%) for the various molar ratios of fatty acid to alcohol studied. With H_2SO_4 as catalyst, the yield was as high as 89.8% at 65 °C after 5 h. The fatty acids profile of the oil (palmitic acid: ~12%; stearic acid: ~8%; oleic acid: ~52% and linolenic acid of 17%) and the different reactivities of the acids were responsible for the observed differences in conversion to methyl esters. The findings attained with this study might contribute to the economic utilization of a non-edible feedstock.

1. Introduction

Fatty acid methyl esters (FAME) (biodiesel), obtained from vegetable oils of edible and non-edible sources, have been introduced as a promising substitute to fossil fuels. Their combustion is environmentally more benign than that of petroleum-based fuel, they offer less storage difficulties, have a high cetane number and flash point and possess excellent lubrication characteristics (Hameed et al., 2009; Mustafa, 2007). FAME is typically synthesized via catalytic transesterification and/or esterification of animal fats, vegetable or waste cooking oils with short chain alcohols (mostly methanol). The high value of edible vegetable oils as a food product makes their utilization for the synthesis of cost-effective FAME very challenging (Canakaci and Gerpen, 2001). Furthermore, if edible oil is employed in biodiesel industry, the world food market is affected. Biodiesel is also expensive due to such issues as equipment and processing conditions (Asakuma et al., 2009; Szulczyk and McCarl, 2010). Thus, the utilization of such oils for biodiesel production in some developing countries with limited arable land per capita is not economic or even prohibited (Lin et al., 2011). In order to address the shortages of feedstock for the production of biodiesel, new non-edible oil sources need to be exploited (Lin et al., 2011; Mustafa, 2011). For example, karanj (*Pongamia pinnata*) oil, a high fatty acid non-edible oil can be employed to produce biodiesel (Sharma and Singh, 2008; Naik et al., 2008; Nabi et al., 2009).

Crude karanj oil (CKO) is extracted from the seeds of the plant, and has found applications in body oils, salves, lotions, soaps, hair tonics, shampoos and pesticides (Kesari et al., 2010). This enduring plant thrives in tropical conditions and is now found in India, Malaysia, Thailand, Vietnam, Australia, Florida, Hawaii, The Seychelles, Oceania and The Philippines (Mukta and Sreevalli, 2010). CKO is considered to be less toxic and cheaper than jatropha oil, so it has become the subject of biodiesel research (Karmee and Chadha, 2005; Naik et al., 2008; Sharma and Singh, 2008).

The industrial value of vegetable oils depends on their fatty acids composition and the ease with which it can be modified (Berchmans and Hirata, 2008; Ramos et al., 2009). CKO contains no less than 23% saturated fatty acids (myristic, stearic and palmitic acid) and more than 73% unsaturated fatty acids (oleic, linoleic and arachid oleic acid). For example, it contains more mono-unsaturated oleic acid (51.59%) than other non-edible oils such as tung oil (8.0%), jojoba oil (11.0%), neem oil (45.55%) and jatropha oil (44.7%). While feedstock with a low level of free fatty acids (FFAs) can be alkali catalyzed during the biodiesel production process, feedstocks with significant FFAs amounts perform better in the presence of acid catalysts (Demirbas, 2009).

Thus, the present study investigated FAME synthesis using non-edible, high fatty acid CKO under mild conditions by employing conventional Brönsted acids, sulfuric and phosphoric acid as homogeneous catalysts in the esterification of CKO with methanol.

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2. Methods

2.1. Chemicals and physiochemical properties of karanj oil

Crude karanj oil (CKO) was supplied by TelagaMadu Resources Ltd., Malaysia. Sulfuric acid (95–98%) was purchased from R & M Chemicals, Ltd. Malaysia. Phosphoric acid (85 wt.%) and GC-grade heptane were supplied by Sigma–Aldrich, Malaysia. Methanol of highest purity (99.9%) and GC-grade hexane were obtained from Merck, Germany. All the received chemicals were used without any further purification or treatment. The characteristics of the as obtained CKO are presented in Table 2.

2.2. Reaction of CKO with methanol

Reactions of CKO with methanol using H_2SO_4 as a homogeneous catalyst were carried out under reflux by using a system of four round bottom flasks, each of 250 mL, mounted on heating mantles and connected to overhead condensers in series and equipped with digitally controlled magnetic stirrers. In a typical synthesis, a known amount of H_2SO_4 (0.5−3.5%), based on oil mass, was mixed with 16.64–35.55 mL of methanol and charged along with 88.842 g of CKO (total volume not exceeding 150 mL) into the reactor and stirred at 600 rpm. The composition of the products was analyzed by a gas chromatograph (GC; Shimadzu 2010 plus, Japan) equipped with a flame ionization detector (FID) and using a Nukol capillary column (15 m × 0.53 mm × 0.5 μm). Similarly, in order to compare the catalytic performance of H_2SO_4, an analogous experiment was conducted using H_3PO_4 as homogeneous catalyst adopting molar ratio of oil/methanol of 1:6 and allowed to proceed for 5 h at 65 °C. The reactions were carried out at temperatures ranging from 55 to 70 °C, monitored with a thermocouple sensor attached to a digital control interface for different reaction times. At the completion of the experiment, the reaction mixture was left to settle for 2 h before being transferred to a 15 mL centrifuge tube and methyl ester was separated using a centrifuge at 2000*g* for 15 min. Once the two phases were separated, the excess alcohol in each phase was recovered and re-used.

Table 1
Properties of crude karanj oil (CKO) before esterification and test methods used.

Properties	Karanj oil	Test method
Density, g/mL 15 °C	0.924	EN ISO 3675
Kinematic Viscosity (40 °C), mm^2/s	27.82	EN ISO 3104
Water content,%	10.20	EN ISO 12937
FFA,%	15.62	ASTM D5555
Saponification number, mg/g	186.4	ASTM D5558
Acid number, mg KOH/g oil	31.24	EN14104

The parameters depend on cultivation country and the season of the karanj tree used to produce CKO.

2.3. Analysis of products

The conversion of CKO to biodiesel was valuated as a molar ratio of produced FAME per mole of feedstock. The evaluation was based on the determination of FAME content in the product as measured by GC analysis according to the EN14103 standard technique (Munari et al., 2007).

The analysis used methyl heptadecanoate as internal standard. The internal standard (IS) solution was prepared as 10.0 mg/mL of methyl heptadecanoate (C17:0) in heptane. The sample was prepared by adding 20 μL of reaction sample to 250 μL of IS solution. The injector and detector temperatures were fixed at 250 °C, whereas the oven temperature was set isothermally at 210 °C. Helium at 1.3 mL/min was used as carrier gas. A volume of 1 μL of the FAME sample containing IS solution was injected to the GC, and the FAME content was calculated according to (Munari et al., 2007).

3. Results and discussion

3.1. Effect of catalyst amount on CKO esterification

Fig. 1 shows the FAME content produced from CKO esterification when H_2SO_4 or H_3PO_4 was applied as liquid catalyst. When the catalyst amount was varied from 0.5% to 3.0%, a higher FAME yield was obtained with H_2SO_4 than H_3PO_4. The H_2SO_4-catalyzed process attained a maximum FAME content of 89.8% at a catalyst dosage of 2.0% sulfuric acid compared to a 15% yield when using 2% H_3PO_4. It was noted that addition of more than 2% sulfuric acid darkened the color of the product but amounts lower than 2% reduced the FAME yield.

3.2. Effect of alcohol to oil molar ratio

Alcohol/oil molar ratio was an important parameter controlling the conversion of triglycerides to methyl esters (Demirbas, 2009). Theoretically, the esterification reaction requires three moles of alcohol for each mole of oil; however, in practice, the molar ratio of the oil should be in excess of the stoichiometric ratio in order to drive the reaction towards ester formation. Fig. 2 presents the influence of different molar ratios (methanol/oil) on FAME yield using either H_2SO_4 or H_3PO_4. A ratio in the range of 4:1–8:1 was applied and, despite the low ratio of 6:1, the total methyl esters yield

Table 2
Properties of karanj oil methyl esters and test methods used.

Property	CKO methyl ester	EN 14214/ASTM limits	Test methods
Acid value, KOH, mg g^{-1}	0.17	0.5 max	EN14104
Water content,%	0.038	0.05% max	EN ISO 12937
Kinematic viscosity (40 °C), mm^2/s	4.66 ± 0.02	3.50–5.00	EN ISO 3104
Cloud point, °C	6	NS[a]	EN14214
Pour point, °C	3	NS[a]	ASTM D 97
Flash point, °C	212	120 min	EN22719
Density (15 °C), g cm^{-3}	0.883	0.860–0.900	EN ISO 3675
Group 1 metals (Na + K), mg/kg		0.5	EN14214
Refractive index (at 40 °C)	1.478	NS[a]	Atago refractometer model RX-5000a
Free glycerin, wt.%	0.0064	0.02	ASTM D6584
Total glycerin, wt.%	0.082	0.240	ASTM D6584
Phosphorus, mg/kg	0.04	<4–10	ASTM D4951
Monoglyceride content, wt.%	2.63	<0.8	EN14214
Diglyceride content, wt.%	0.78	<0.2	EN14214
Triglyceride content, wt.%	0.06	<0.2	EN14214

[a] NS: not specified.