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Performance of Refined and Waste Cooking Oils derived from Palm Olein on Synthesis Methyl Ester via Mechanical Stirring

[1]Lai Fatt Chuah, [1]Suzana Yusup, [2]Abdul Rashid Abd Aziz, [1]Awais Bokhari

[1]*Chemical Engineering Department, Center of Biofuel and Biochemical Research (CBBR), Biomass Processing Cluster, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Seri Iskandar, Perak, Malaysia*
[2]*Mechanical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Seri Iskandar, Perak, Malaysia*

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ABSTRACT

The present work highlights the potential raw materials for biodiesel production derived from the refined cooking oil and waste cooking oil– originated from refined cooking oil. The effect of impurities in waste cooking oil was investigated by comparing to the refined cooking oil via transesterification with oil to methanol molar ratio of 1:6 in the presence of 1 wt. % potassium hydroxide as alkali catalyst at 60 °C operating temperature. It is observed that more than 96.5 % of refined and waste cooking oils have been converted to methyl ester in 90 min with yield efficiency of 0.15 x 10^{-4} and 0.14 x 10^{-4} g/J. All the waste cooking oil methyl ester and refined cooking oil methyl ester properties were found to meet with the EN 14214 and ASTM D 6571 standards.

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INTRODUCTION

Biodiesel is an alternative fuel to replace the petroleum diesel (Chuah *et al*., 2015a). Biodiesel can be produced from various sources, such as edible oil, non-edible oil, animal fat and algae (Ahmad *et al*., 2014). About 95 % of world biodiesel production is derived from edible oils (Silitonga *et al*., 2013). However, it has strongly opposed by non-government organisation worldwide due to its negative impact as it competes with food for resources (Tan *et al*., 2011). Consumption of edible oil in biodiesel production has led to the price of edible oil and biodiesel to increase to levels 1.5 to 2 fold higher than diesel fuel (Maddikeri *et al*., 2012). In this regard, non-edible waste cooking oils become more attractive and promising alternate raw material for biodiesel production. Waste cooking oil is considerably cheaper - five times average lower than refined cooking oil (Chuah *et al*., 2015b). Malaysia is diversifying its biodiesel feedstock towards non-edible oil, such as waste cooking oil (WCO) derived from palm oil. Malaysia is the second largest producer of palm oil in the world. Around 29 Mt/y of WCO is produced and about 4.1 kg is generated per person/y worldwide (Maddikeri *et al*., 2012). The Malaysian population is reaching 30 million persons and around 0.12 Mt/y of WCO is generated. By utilising WCO in biodiesel production is a clean technology solution offering solutions for both disposal and health problems, e.g. feeding mixture for domestic animal, reusing and recycling (Chuah *et al*., 2015b). The energy efficiency and raw material cost are major contribution to the total cost of biodiesel production. The main purpose of this work is to study the effect of impurities in WCO on the performance of conversion and yield efficiency via mechanical stirring with oil to methanol molar ratio of 1:6 in the presence of 1 wt. % potassium hydroxide as alkali catalyst at 60 °C operating temperature. The conversion and yield efficiency performance of WCO was compared with refined cooking oil (RCO) to examine the effect of impurities in WCO. In addition, qualities of refined cooking oil methyl ester (RCOME) and waste cooking oil methyl ester (WCOME) produced via mechanical stirring have been investigated according to the ASTM D 6751 and EN 14214 standards.

MATERIALS AND METHODS

The RCO, Alif brand has been purchased from local TESCO Shopping Mall (Seri Iskandar, Perak) at an average price of RM 2.70/L - approximate USD 0.84 in 2015. The Alif cooking oil is derived from the palm olein. WCO was purchased from a local Universiti Teknologi PETRONAS's Cafeteria (Seri Iskandar, Perak) at an average price of RM 0.50/L -

Corresponding Author: Suzana Yusup, Chemical Engineering Department, Center of Biofuel and Biochemical Research (CBBR), Biomass Processing Cluster, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Seri Iskandar, Perak, Malaysia.
E-mail: drsuzana_yusuf@petronas.com.my, +605-3687642

approximate USD 0.14 in 2015. WCO originates from palm olein. WCO has passed through 3 to 5 cycles of heating between 180 - 200 °C and cooling about 25 - 40 °C to fry food. WCO was first filtered through a normal sieve to remove the suspended particles. The filtered WCO was stirred and heated at temperature between 105 and 110 °C for 1 h in order to remove the water in the oil. The WCO was allowed to cool down at room temperature and thus store it in a container for further process. The properties of RCO and WCO are illustrated in Table 1.

The dissociation of triglyceride was analysed following EN 14103 standard method and using the GC-FID (Agilent Technologies, 7890A GC System) and capillary column methylpolysiloxane (DB-23) (60 m x 0.25 mm x 0.25 μm). The temperature program starts at 100 °C, holding for 2 min, heating at 10 °C/min until 200 °C, heating at 5 °C/min until 240 °C and finally holding for 7 min. Helium was used as a carrier gas at the flow rate of 4 mL/min. The hydrogen and air were used at flow rate of 50 mL/min and 400 mL/min for the flame production. All experiments were repeated in three times and the reported values are averages of the individual runs and the inaccuracy percentage were less than 2 % of the average value. The results presented in the graph were the average results. The properties of the purified biodiesel were analysed according to the ASTM and EN standards (Chuah *et al*., 2015b).

Table 1: Characterisation of refined and waste cooking oils

Parameter		mean ± standard deviation (n=3)	
		Refined cooking oil	Waste cooking oil
Acid value (mg KOH/g)		0.19 ± 0.03	2.04 ±0.03
Saponification value (mg KOH/g)		190.74 ± 1.40	204.77 ± 1.40
Molecular weight (g/mol)		882.47 ± 6.49	822.03 ± 5.63
FFA (%)		0.09 ± 0.02	1.02 ± 0.02
Higher heating value (MJ/kg)		38.49 ± 0.05	39.96 ± 0.04
Density (g/cm^3)	at 20°C	0.91347 ± 0.00003	0.91567 ± 0.00003
	at 40°C	0.89976 ± 0.00003	0.90195 ± 0.00004
	at 60°C	0.88627 ± 0.00003	0.88844 ± 0.00003
Kinematic viscosity (mm^2/s)	at 20°C	116.90 ± 0.07	124.00 ± 0.01
	at 40°C	48.86 ± 0.06	51.04 ± 0.03
	at 60°C	25.23 ± 0.02	26.28 ± 0.02
Peroxide value	(meq/kg)	1.23 ± 0.06	7.13 ± 0.12
	(mg/g)	9.87 ± 0.46	57.07 ± 0.92
Oxidative stability (h)		20.61 ± 0.21	18.71 ± 0.04
Iodine value (g I_2/100 g)		59.47 ± 0.78	57.70 ± 0.53
Moisture content (wt. %)		0.04 ± 0.00	0.12 ± 0.00
Flash point (°C)		315 ± 1	309 ± 1
Mono, Di and Triglycerides (wt. %)	Monoglycerides	0.10 ± 0.04	0.10 ± 0.04
	Diglycerides	1.20 ± 0.05	3.47 ± 0.15
	Triglycerides	98.70 ± 0.10	96.43 ± 0.35
Fatty acid composition (wt. %)	Myristic acid, C14:0	0.97 ± 0.01	0.98 ± 0.01
	Palmitic acid, C16:0	37.94 ± 0.36	39.02 ± 0.35
	Stearic acid, C18:0	4.21 ± 0.03	4.52 ± 0.28
	Oleic acid, C18:1	45.08 ± 0.26	44.57 ± 0.62
	Linoleic acid, C18:2	11.80 ± 0.17	10.91 ± 0.10

The homogenous transesterification reaction were carried out using an electrothermal mantle with temperature controller, two-neck round bottom flask of 500 mL capacity with a reflux system and a magnetic stirrer. An appropriate quantity of WCO was heated up to 60 °C in the round bottom flask by electrothermal mantle. The experiments were carried out under reaction conditions of reaction temperature of 60 °C, oil to methanol molar ratio of 1:6, 1.0 wt. % of KOH catalyst and reaction time of 90 min. The speed of the stirrer was kept constant at 600 rpm for all test runs. For comparison purpose, RCO was also transesterified using similar conditions and method describe above. The completed reaction of mixture was allowed to settle down in separating funnel by gravity settling for 4 h. The by-products and catalyst were discharged out through the opening of the funnel. The products were washed with the deionised warm water at 40 °C to remove residual catalysts and other by-produces until the water pH became neutral. The remaining methanol and water in the product was evaporated under rotary vacuum evaporator. To ensure the sample is water free, a 1 g of sodium sulphate anhydrous was added into the product. The product was shaken for 1 min and then the content was filtered by filter paper (541 Whatman). The conversion performance of the triglyceride dissociation into methyl ester in the products was measured by using GC-FID analysis. Experiments were conducted in three replicates to determine the range and reproducibility of the results.

RESULTS AND DISCUSSION

Two feedstock oils were selected - RCO and WCO derived palm olein in the present work for biodiesel production by using mechanical stirring. The reaction time, conversion and yield efficiency of RCO and WCO by using oil to methanol molar ratio of 1:6 with the present of 1 wt. % potassium

hydroxide (KOH) at 60 °C operating temperature have been compared as shown in Table 2. It is observed that there is no significant different of yield efficiency between both biodiesel by mechanical stirring. The impurities of the WCO - originated from RCO in present study did not influence the yield efficiency, reaction time and methyl ester conversion due to the good quality of the collected WCO. It can be found that about 90 min of reaction time is required for both feedstock oils via mechanical stirring to archive more than 96.5 % conversion. The yield efficiency of refined cooking oil methyl ester and waste cooking oil methyl ester were 0.15 x 10^{-4} and 0.14 x 10^{-4} g/J.

Table 2: Comparative of refined and waste cooking oils on reaction time, conversion and yield efficiency

Feedstock	Reaction time (min)	Conversion (wt. %)	Yield efficiency (g/J) x 10^{-4}
Waste cooking oil	90	97	0.14
Refined cooking oil	90	98	0.15

In order to make biodiesel to be commercialised, it shall meet a set of requirements defined in ASTM D 6751 and EN 14214 standard specifications. These standards indicate the allowable contaminants concentration in pure biodiesel (B100), along with other chemical-physical properties necessary for a safe and satisfactory engine operation. The fuel properties of WCOME and RCOME were analysed by referring to both standards is shown in Table 3. It is observed that the acid value is an indication of the age and quality of the fuel. The results revealed that the acid values of RCOME and WCOME was 0.08 and 0.33 mg KOH/g, which is 27 and 110 fold higher compared to diesel fuel based petroleum. However, both of them satisfied the standards. The density of the RCOME and WCOME produced from mechanical stirring was similar, i.e. 0.88 g/cm3 at 15 °C and it complied with the EN 14214. The kinematic viscosities of RCOME and WCOME were 4.73 and 4.67 mm^2/s at temperature of 40 °C were within the standards. Therefore, no further modification of diesel engine is needed as there is no significant different compared to the viscosity of diesel fuel based petroleum, which is 3.65 mm^2/s. Both RCOME and WCOME produced via mechanical stirring were resulted in more than 96.5 % methyl ester conversion. Oxidation stability (OS) is one of the important fuel properties that influence the storage and usage efficiency. It is well known that most of the biodiesel derived from many common raw materials are very hard to meet the OS requirement of EN 14214 due to high percentage of unsaturated fatty acids content (Fernandes *et al*., 2014), unless antioxidants are added to the biodiesel (Ramos *et al*., 2009). Rizwanul Fattah *et al*. (2014) reported that by adding antioxidants, could significantly reduce nitrogen oxides (NOx) emissions. The poor OS of the biodiesel may also be influenced by many factors, such as the presence of air, heat, metal, traces, peroxides and light during storage (Bajpai and Tyagi, 2006). However, both biodiesels satisfied the minimum limits of EN 14214, but about 5.5 – 5.7 fold lower than diesel fuel. Cetane number (CN) is an ability of the fuel to ignite quickly after being injected and a higher value indicates better ignition quality of fuel. The CN in the present study was found to be 59 – RCOME and 60 – WCOME, which are within the standards. Iodine value (IV) is much influenced the OS and the formation of deposits in diesel engine injectors (Wang *et al*., 2012). Altun (2014) reported that the lowest IV value of biodiesel is indicating highest CN and consequently reduced NOx emissions. The minimum requirements of IV are 120 g I_2/100 g in EN 14214 standard. Both biodiesels met the IV standard, being on average half the allowable value in the EN standard. Overall, the fuel properties obtained from WCOME and RCOME were found to meet the minimum requirement of EN 14214 and ASTM D 6571 as depicted in Table 3.

Table 3: Properties of produced biodiesel and diesel fuel

Parameter	RCOME	WCOME	Diesel fuel	EN 14214	ASTM D 6751
Acid value (mg KOH/g)	0.08	0.33	0.003	0.5 ≥	0.8 ≥
Density (g/cm^3) at 15 °C	0.88	0.88	0.85	0.86-0.90	-
Kinematic Viscosity (mm^2/s) at 40 °C	4.73	4.67	3.65	3.5-5.0	1.9-6.0
Ester Content (wt. %)	97.4	97.2	-	96.5 ≤	-
Oxidative Stability (h), 110 °C	7.34	7.56	41.77	6 ≤	-
Cetane Number	59	60	47	51 ≤	47 ≤
Iodine value (g I_2/100 g)	60	58	-	120 ≥	-

Conclusion:

Biodiesel as a green alternative fuel produced from renewable waste resources is a very attractive option to replace petroleum based diesel fuel. Biodiesel derived from waste oil can be a very promising alternative feedstock, which could reduce

the disposal problems, production cost and global emission management cost as a lower pollutant emission. Impurities of the WCO in present study did not significant different on the yield efficiency, reaction time and conversion. Utilising WCO for biodiesel production is a sustainable and further solution to mitigate health and disposal issues. Moreover, the present study shows that the produce biodiesel derived from WCO and RCO meet the both standards of EN 14214 and ASTM D 6751. Further research must be carried out on different intensification process, such as hydrodynamic cavitation and ultrasonic cavitation in terms of energy efficient, time saving, cost, ecofriendly and scale up make biodiesel production viable for industrial scale.

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