Production of Biodiesel from Locally Available Spent Vegetable Oils

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Abstract - The depletion of fossil fuels prompted considerable research targeting the development of alternative fuel sources. Biodiesel production has acquired increasing importance owing to its renewable nature and milder environmental impacts. To this end, alternative sources of feedstock have been sought and studies aiming at the optimization of the production procedure have been carried out. Millions of liters of waste frying oil are produced from local restaurants and houses every year, most are discarded into sewage systems damaging networks and complicating the treatment process. This study is intended to consider aspects related to the feasibility of the production of biodiesel from waste frying oils in order to alleviate the waste frying oil pollution problems as well as to reduce the cost of biodiesel production. Locally available spent vegetable oils have been collected from different sources and accordingly have somewhat different chemical compositions. The conducted experiments involved the production of biodiesel from the different feed stocks using the base catalyzed trans-esterification process. The quality of the produced biodiesel is compared to petro-diesel in terms of established standard specifications.

I. INTRODUCTION

Increase of energy usage in the industrialized world entails rapid depletion of nonrenewable fossil fuels and is associated with pollution problems [1]. Renewable resources of energy include solar energy, wind energy, geothermal energy, tidal energy, ocean thermal energy, hydropower, and alternative combustible fuels [2]. Production of alternative fuels should be technically feasible, economically competitive, environmentally acceptable, and readily available [1]. Diesel engines are the main engines used in industrial, transport and agricultural applications due to their high efficiency and reliability [3]. Diesel engines operate via compression ignition where the fuel is injected in the engine's cylinder with compressed air at high pressure and temperature. The fuel self-ignites and burns rapidly when it enters the cylinder forcing the piston back down and converting the chemical energy in the fuel into mechanical energy. The fuel used in the first diesel engine, developed by Dr. Diesel in 1895, was vegetable oil. This, however, poses socio-economic arguments arising from the conflict between food shortage and the demand for energy. Due to the availability and low cost of petroleum diesel fuel, vegetable oil-based fuels are not used widely except in times of high oil prices and shortages as in World War II and the oil crisis of the 1970's. At present, vegetable oils are not directly used as alternative fuels due to their high viscosity, incomplete combustion, injection and ring coking and may ultimately cause engine failure [4, 5]. Vegetable oils, as a source of biodiesel production, include sunflower, safflower, soybean, cottonseed, rapeseed, and peanut oils. Vegetable oil based fuels are the attractive alternative for diesel fuel due to their renewable nature, better ignition quality, comparable energy content, high density, higher flash point, nontoxic emissions, cleaner burning, nearly zero sulfur content, high cetane number and high calorific value close to diesel fuel [6, 7].

There are many reasons that encourage search for alternative compression ignition engine fuels. Conventional diesel engine fuels are associated with smoke and nitric oxide (NOx) emissions. More stringent governmental regulations targeting cleaner combustion have been imposed to reduce diesel engine emissions. This can be done by engine development with fuel reformulation and use of alternative fuels [3]. The alternative sources considered include oils of plant origin [1]. Bio-fuel, namely biodiesel and ethanol, is predicted to replace petroleum diesel fuel [8]. The ethanol is used for gasoline engines and biodiesel for compression ignition engines [9]. Many countries such as Brazil, the United States, Germany, Australia, Italy and Austria are currently using bio-fuel; however, its economic feasibility should be improved before it could be widely used. In most countries, the governments support biodiesel usage by reducing its

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cost through tax rebates [10]. According to the American Society for Testing and Materials (ASTM), biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils and animal fats. "Bio" represents its biological and renewable source, and "diesel" implies its use as a fuel on diesel engines [11]. Biodiesel is derived from renewable biomass sources thus it represents a closed carbon dioxide cycle (approximately 78%) [12].

The chemical structure of methyl esters depends on the length and degree of un-saturation of the fatty acid alkyl chains. The degree of un-saturation of methyl esters affects the carbon to hydrogen ratio which is slightly different from conventional diesel fuel. The oxygen content is the important difference between conventional diesel fuel and biodiesel because biodiesel contains 10-12 wt% oxygen [13, 14, 15]. The burning efficiency of biodiesel is improved due to its high oxygen content; thus, it corresponds to lower particulate matter (PM), carbon monoxide (CO), and hydrocarbon (HC) emissions, however, and it produces higher NOx emissions [16].

The purpose of this work is to conduct a laboratory scale study for production of biodiesel using locally gathered waste vegetable oils from different origins. The processing requirements for the different feed stocks are to be compared. The final product specifications are to be also compared with those of petro diesel.

II.   EXPERIMENTAL CONDITIONS

Trans-esterification reactions have to be carried out under vigorous mixing conditions owing to the immiscibility of the oil and methanol phases. Since trans-esterification is a relatively slow process, intense mixing is required both because of the relatively high oil viscosity and in order to ensure sufficient interfacial area between the two reactants present in different phases. The optimum operating temperature for this reaction is 65°C, which is slightly above the boiling point of methanol (64.7°C)[17]. When the reaction temperature exceeds the boiling point of methanol, the methanol will vaporize and form a large number of bubbles which may inhibit the reaction. The experimental conditions for the different feed stocks have been fixed at an agitation rate of 400 rpm and at a temperature of 65°C.

III.   MATERIALS AND METHODS:

Waste oil was collected from three different sources: (1) waste frying palm oil (WPO) from a local fast food restaurant, (2) mixed waste home frying oil used only once or twice (WHO), (3) waste mixed oils, sunflower, palm oil and soya oil (WTO) collected after 48 working hours from a controlled food court.   The chemicals used in the experiments were: methanol procured from El-Nasr Pharmaceutical Chemicals Co. (ADWIC) with a molecular weight of 32.04 and an assay of 99.8%, KOH purified pellets from Thann-Fransu, analar grade isopropyl alcohol, and phenolphthalein.

A small-scale laboratory setup was used for pretreatment and trans-esterification experiments. The waste oil is first heated to 60°C in a water bath to ensure complete melting. It is then filtered using a standard Buchner funnel connected to a vacuum pump in order to ensure complete solids removal. The filtrate is then heated in a water bath up to 110°C to ensure vaporization of any residual water since the presence of water negatively affects the reaction by promoting saponification and increasing the viscosity. Trans-esterification experiments were conducted in triplicate using 100g of used frying oil. Methanol and KOH catalyst were poured into a clean reaction flask provided with a magnetic stirrer and a reflux condenser. The oil, methanol, and KOH mixture was stirred for 120 min at 60-70°C and 400 rpm. The trans-esterification reaction was carried out for different ratios of oil to methanol (10, 15, 20, 30, and 40g). The amount of catalyst had a pronounced influence on the conversion to esters. Various amounts (0.75g, 1g, and 1.5g) of KOH catalyst were used in the experiments: After the trans-esterification reaction, the biodiesel was separated from glycerol using a separating funnel where the reaction mixture was allowed to cool. Clear separation was observed after 12-24 hours of settling. The ester was then washed three times with warm distilled water. The product was then dried by heating at 110°C for 30 min to remove the moisture content and the methyl ester is filtered to remove any residual soap.

The effects of catalyst content, methanol to oil molar ratio, and reaction time were determined. It is recognized that the production of waste cooking oil will be a function of the frying temperature and length of use as well as the material used for frying.
The free fatty acid (FFA) analysis for the raw oil

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should be lower than 0.5%. The oil has been treated and the FFA content was determined by standard titration while the fatty acid composition was determined using chromatographic analysis (GC).

IV.   RESULTS AND DISCUSSION:

• Yield and Conversion

The effect of base-catalyzed trans-esterification process variables on biodiesel yield from the different waste frying oils was investigated by changing the (KOH) catalyst to oil ratios (% w/w) and the methanol to oil ratios (% w/w).

Table 1.Yield and Conversion of Trans-esterification Reaction of all Waste Frying Oils

Run#	KOH (g)	Meth. (g)	Yield %			Conversion %		
			WPO	WTO	WHO	WPO	WTO	WHO
1	0.75	10			63.69			32.41
2	0.75	15	81.41	67.25	78.22	76.92	55.56	61.38
3	0.75	20	76.21	86.35	87.71	61.54	55.56	61.03
4	0.75	30	87.05	75.73	85.14	76.92	77.78	62.07
5	0.75	40	90.26	88.06	87.25	76.92	66.67	31.72
6	1	10	34.53		71.18	69.23		60.34
7	1	15	77.53	54.2	91.06	61.54	55.56	42.07
8	1	20	87.18	80.04	91.41	69.23	55.56	80.69
9	1	30	84.66	83.27	88.01	84.62	77.78	42.76
10	1	40	88.26	84.08	68.96	84.62	55.56	42.17
11	1.5	10	45.9			69.23		
12	1.5	15	70.66	73	83.89	38.46	55.56	50.35
13	1.5	20	78.19	79.4	72.37	61.54	66.67	42.41
14	1.5	30	88.59	77.12	67.85	76.92	77.78	60.21
15	1.5	40	81.64	89.6	54.48	53.85	83.33	42.05

Table 1 presents the calculated yield and conversion obtained from the experimental data for the different waste frying oils under different reaction conditions.

Previous results reported in the literature [17] on the effect of catalyst and methanol to oil ratio on biodiesel production suggest that biodiesel with the best properties was obtained using 1 % KOH by weight as the catalyst. Methanolysis with this catalyst produced the best yields and viscosities of the resulting esters. A. B. Chhetri et al. [12] used 0.4%, 0.6%, 0.8%, 1.0% and 1.2% sodium hydroxide as a catalyst and observed that no reaction took place with the 0.4% NaOH. With catalyst concentrations of 0.6%, 0.8% and 1.0%, ester yields were approximately 50%, 94% and 40%, respectively. It was also observed that the ester yield decreased with the increase in NaOH concentration. With 1.2% catalyst concentration, soap

formation was pronounced. Increased soap formation caused the ester to dissolve into the glycerol layer.

The findings obtained in the present work may be compared with the above literature data by considering the experimental results presented in Figures (1-3) below. Figure (1) presents the yields obtained for WPO, WHO, and WTO respectively for different amounts of CH_3OH and KOH.

It is seen that the highest yield for WPO ranged between 87.05% to 90.26% (runs 4, 5, 8, 10, and 14). In these runs, the dominant catalyst amount ranged between (0.75 – 1g) except for run 14 which used 1.5g KOH. Two runs (runs 6, 11) gave a very low yield (34.53%, 45.9%) and no yield was obtained for run (1). All of these runs were carried out using 10g CH_3OH, and as such the amount of methanol is not sufficiently in excess to increase the rate of the forward reaction towards ester production.

The maximum yield for (WHO) was found in runs (7, 8, 9) where the amount of catalyst was (1g) and the amount of methanol was (20, 15, 30g), respectively. No yield was obtained from run number (11) while the lowest yield was obtained in runs (1, 10, 14, and 15), where the high amount of KOH (1.5g) reduced the yield due to saponification (runs 14, 15) and the low amount of methanol caused incomplete reaction (run 1). Also the increase of methanol reduced the yield because it diluted the reaction mixture (runs 10, 14 and 15).Thus the optimum trans-esterification reaction conditions for (WHO) were 1g KOH and 20g methanol.

The maximum yield for (WTO) was in runs (3, 5, 9, 10, and 15) with KOH ranging between 0.75g and 1g except for run 15 which used 1.5g KOH. The lowest yield was in runs (2, 7) and no reaction took place in runs (1, 6, and 11). All of these runs were carried out with methanol ranging between (10 – 15g), and this means that the amount of CH_3OH should not be lower than (20g) to push the reaction in the forward direction. Thus, in the case of using (WTO) the optimum amount of CH_3OH required to achieve a high yield is (20g).

Comparison of the yields of the three types of oil showed that the highest yield was obtained for (WHO) in runs (8, 7) reaching 91.41% and 91.06%, respectively. This is attributable to that (WHO) had the lowest FFA content and thus it gave higher yields

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under the same conditions. The second highest yield was obtained in run (5) for (WPO). Yields for both (WPO) and (WTO), at low amounts of CH₃OH (10 – 15g), were very low and sometimes no reaction occurred.

The highest conversion of 84.62% was obtained for (WPO). The second highest conversion of 83.33% was for (WTO) while the highest conversion using (WHO) was 80.69%.
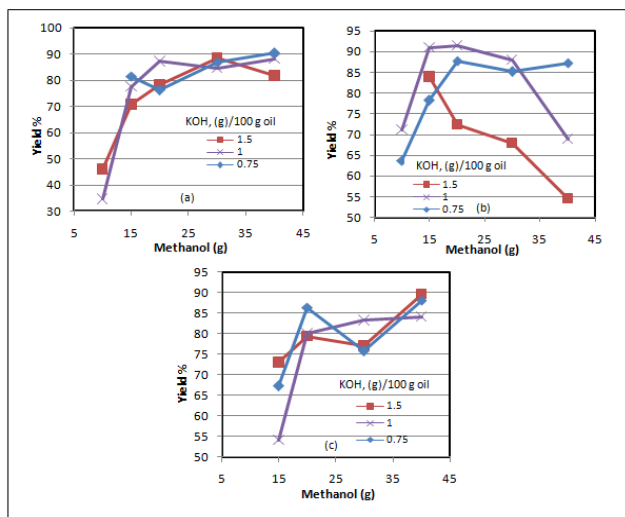

Fig .1. Effect of catalyst content on yield (a) WPO, (b) WHO and (c) WTO

- **Density and Viscosity**

Table 2 presents the density and viscosity of the produced Fatty Acid Methyl Ester (FAME) from WPO, WHO, and WTO respectively for different amounts of KOH and CH₃OH. The FAME density should lie between 0.86 and 0.9 kg/m³ [11]. All the (WPO) densities were within the above specified range except for run (10) which gave a lower density (0.849 kg/m³). All the measured (WTO) and (WHO) densities were equal to or higher than the upper limit of the specification. Figure (2) displays the measured kinematic viscosities (KV) for the FAME produced from WPO, WHO, and WTO, respectively. The range for biodiesel kinematic viscosity is (1.9 – 6 mm²/s) according to ASTMD 6751 standard and (3.5 – 5 mm²/s) accords to EN14214 standard. The measured (KV) at 40°C for (WPO) was 52.9 mm²/s, for (WHO) was 33.5 mm²/s, and for (WTO) was 52.1 mm²/s. Most of the produced FAME was within the ASTM range except for run (1) for (WHO) and runs (2, 3, 7, and 12) for (WTO). In these runs, low amounts of methanol were used and as such (WTO) require

more methanol to improve FAME characteristics. For (WPO) the out of specification runs were (2, 6, 7, 11, and 12). All of these runs were carried out using low amounts of methanol and, accordingly, their viscosities were higher than the standards. Palmitic acid was the major saturated fatty acid found in this waste oil which is the major factor that determines the viscosity of biodiesel. Finally, the recorded decrease in density and viscosity after trans-esterification indicates that good trans-esterification has been achieved under appropriate experimental conditions.

Table 2.Density and Viscosity of FAME from all Waste Frying Oils

| Run#	KOH (g)	Meth. (g)	Density kg/m³			Viscosity mm²/s		
			WPO	WTO	WHO	WPO	WTO	WHO
1	0.75	10			0.91			6.6
2	0.75	15	0.889	0.92	0.91	6.14	9.2	5.6
3	0.75	20	0.8924	0.91	0.91	5.63	6.7	4.8
4	0.75	30	0.8856	0.90	0.90	4.88	5.2	4.6
5	0.75	40	0.8844	0.90	0.90	5.05	4.9	4.5
6	1	10	0.899		0.90	8.31		5.1
7	1	15	0.891	0.91	0.91	6.11	8.7	4.9
8	1	20	0.8818	0.90	0.90	5.08	4.9	4.4
9	1	30	0.885	0.90	0.90	4.53	4.9	4.2
10	1	40	0.849	0.90	0.91	4.88	5.1	4.7
11	1.5	10	0.896			7.37		
12	1.5	15	0.894	0.90	0.91	6.4	6.6	4.7
13	1.5	20	0.8832	0.90	0.91	4.84	4.9	5.7
14	1.5	30	0.8838	0.90	0.89	4.74	5.1	5.2
15	1.5	40	0.891	0.91	0.90	4.62	5	5
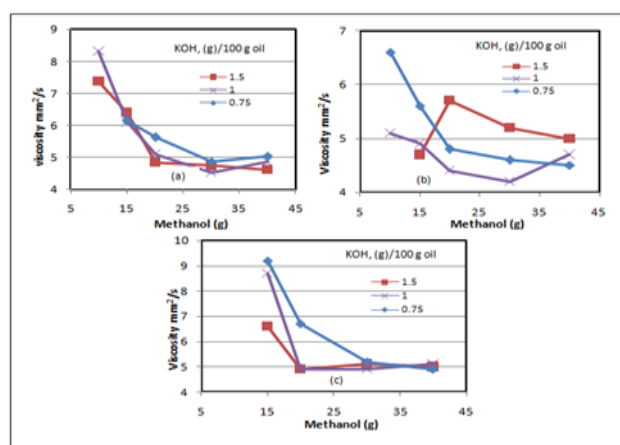
Fig .2. Viscosity of FAME at 40°C, (a) WPO, (b) WHO and (c) WTO

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- **Cloud Point and Pour Point**

Figure (3) reveals that the cloud point for (WHO) ranged between (-2 – 2.5°C), for (WTO) between (-1.75–5°C) and for (WPO) between (15–25°C). The Pour point results presented in Figure (4) revealed that it ranged between (-8 – -3°C) for (WHO), between (-5.5– -0.5°C) for (WTO) and between (4–14°C) for (WPO). It may be concluded that (WPO) is solid at room temperature because its main constituent is Palmitic acid. The FAME produced from (WPO) would not be suitable for cold weather as it will block vehicles' hoses and pipes. The cloud point and pour point limits of Egyptian petro-diesel are 9°C and 6°C, respectively. Thus most esters produced from WHO and WTO would conform to the Egyptian specifications, however all esters produced from WPO would not be suitable for local use in cold conditions.
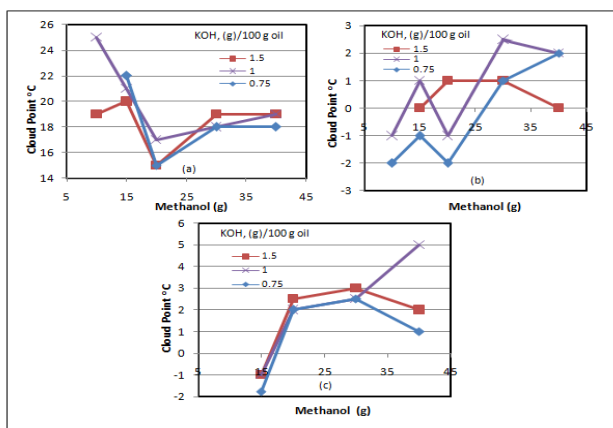

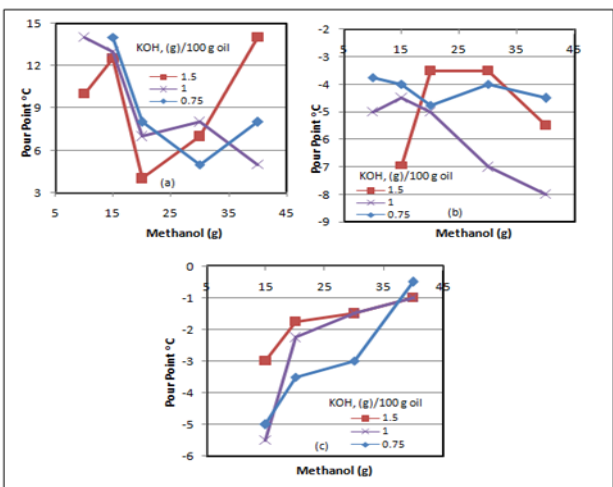Fig .3. Cloud Point of FAME, (a) WPO, (b) WHO and (c) WTO

Fig .4. Pour Point of FAME, (a) WPO, (b) WHO and (c) WTO

V.   SAPONIFICATION VALUE:

The saponification value is defined as the milligrams of KOH required to saponify one gram of oil. The obtained saponification value for biodiesel produced from all the tested waste frying oils (WFO) was higher than that of the WFO feed. This is not the case when virgin vegetable oil is used for biodiesel production. This is attributable to the chemical degradation during frying when reactions such as cyclization and polymerization take place. The saponification value of WPO was160.78 mg KOH/g oil, while that of its esters ranged between 162.69 and 201.96mg KOH/g oil. The saponification value of WHO was150.66mg KOH/g oil, while that of its esters ranged between140.25 and 252.45mg KOH/g oil. The saponification value of WTO was135.25mg KOH/g oil, while that for its esters ranged between145.86 and 238.43mg KOH/g oil. The obtained saponification values for the different oils are presented in Figure (5).
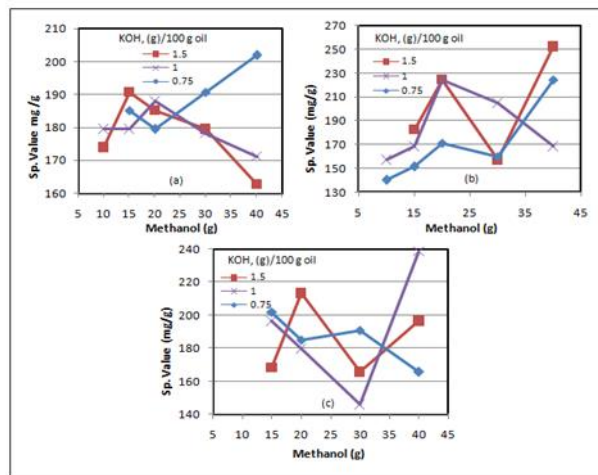

Fig .5. Saponification Value of FAME, (a) WPO, (b) WHO and (c) WTO

I.   GAS CHROMATOGRAPHY (GC) ANALYSIS:

Table (3) presents the results of the GC analysis of the produced FAME from WPO. The fatty acid content is the major factor affecting the properties of biodiesel. The biodiesel derived from the sample of waste cooking oil subjected to GC contained palmitic acid, stearic acid, oleic acid, and linoleic acid. The saturated fatty acid content of the waste cooking oil was approximately 60% corresponding to a Cold Filter Plugging Point (CFPP) of (6-14 ºC).

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Table 3. GC Results of FAME Produced from WPO

KOH (g)	CH$_3$OH (g)	A Palmitate	B Linoleate	C Oleate	D Stearate	Saturated	Unsaturated
0.75	20	49	5.939	38.8	6.202	55.241	44.758
0.75	30	52.7	4.687	36.6	6.008	58.677	41.323
0.75	40	53.2	5.123	35.8	5.878	59.042	40.958
1	20	50	5.913	38.3	5.787	55.745	44.256
1	30	51.8	5.427	37.1	5.744	57.5	42.501
1	40	52.9	5.333	35.8	5.928	58.84	41.161
1.25	20	47.7	6.058	40.2	6.073	53.737	46.264
1.25	30	64.8	4.152	26.6	4.432	69.226	30.775
1.25	40	53	5.232	35.8	6.024	58.982	41.018
1.5	20	57.1	4.854	32.1	5.857	62.996	37.003
1.5	30	53.4	5.31	35.4	5.915	59.294	40.706

II. CONCLUSION

Laboratory trans-esterification experiments have been carried out to determine the effect of the amount of catalyst and methanol on the FAME yield produced from different waste frying oils at a reaction temperature of 60 -70ºC), a reaction time of 120 min and at an agitation speed of 400 rpm. Since the feedstock has been collected from different sources, there was a significant difference in the chemical and physical properties of the produced biodiesel.

The yield, conversion, density, viscosity, cloud point, pour point and saponification value of the produced FAME have been experimentally determined for different KOH and methanol to oil ratios. The optimum amount of catalyst and methanol for the three types of waste oils investigated are respectively(1g KOH – 40g methanol) for (WPO), (1.5g KOH – 40g methanol) for (WTO), and (1g KOH – 20g methanol)for (WHO). The highest yield was obtained from (WHO) due to its relatively low FFA content.

The densities and viscosities of the biodiesel produced from the three waste cooking oils lie within the ASTM standard except for the runs using low amounts of methanol. The cold flow properties of the (WTO) and (WHO) conform to the Egyptian specifications; however, all the esters produced from WPO were not suitable for use in cold conditions. The best biodiesel properties were obtained from (WHO), followed by that obtained from (WTO) and then (WPO) owing to its high palmitic acid content.

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