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Sary Awad, Maria Paraschiv, V. Edwin Geo, Mohand Tazerout. Effect of Free Fatty Acids and Short Chain Alcohols on Conversion of Waste Cooking Oil to Biodiesel. *International Journal of Green Energy*, 2014, 11 (5), pp.441-453. 10.1080/15435075.2012.727926 . hal-00935901

HAL Id: hal-00935901

<https://hal.science/hal-00935901v1>

Submitted on 14 Dec 2022

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EFFECT OF FREE FATTY ACIDS AND SHORT CHAIN ALCOHOLS ON CONVERSION OF WASTE COOKING OIL TO BIODIESEL

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In this article, the transesterification of three types of waste cooking oil (WCO) with methanol and ethanol was studied using alkali catalyzed process. The catalyst used in this study was sodium hydroxide. The effects of temperature, catalyst amount, alcohol to oil ratio, and the time of reaction on the yield were studied. The temperature and the catalyst amount were the most important factors affecting the yield of biodiesel. Also the process exhibited some sensitivity to the level of free fatty acids (FFA) in the WCO and to the type of alcohol. The yields of methyl esters varied from 97% with the lowest acidity (0.4% FFA WCO) to 76% with the highest acidity (3.25% FFA WCO). The ethyl esters yields were lower and the difference increased with the level of FFA in the oil, the maximum yield was 95% and 73% with the lowest and the medium acidities respectively and no reaction was registered with the highest one. The chromatographic analysis of the produced biodiesel showed high contents of fatty acid methyl esters varying from 96.5% to 98%. The physical-chemical characteristics of produced biodiesel were studied and compared to the European norm, EN 14214.

Keywords: *Biodiesel; Waste cooking oil; Transesterification; Methyl ester; Ethyl ester; Free fatty acids*

INTRODUCTION

The world population has increased from 2.5 to 6 billions between 1950 and 2000, and it is expected to reach 9 billions in the four coming decades. This increase of population and the change in their lifestyle demand more energy and raw materials. On the other hand, it generates more wastes that are becoming unbearable by the ecosystem which is dangerously suffering. In Europe, for example, a citizen produces about 600 kg of wastes per year. European parliament has set a law in 2008 for the wastes management which can be resumed by: reusing, recycling, and valorization. The waste cooking oils (WCO) represent a very important share of these wastes, and with the new life style of people and the increasing of fast food share in their nutritional habits, the waste edible oil quantities produced around the world and especially in the big cities are increasing. These wastes are considered as non-dangerous wastes. These wastes should not be landfill or burned into the

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open air, neither poured into the waste water-evacuation networks, but they can be used as raw material in biodiesel-production processes.

The majority of energy consumption for transportation is based on the rapidly depleting fossil fuels resources. So, the studies are focused on new energy sources that can be an alternative to petroleum fuels and that can meet stringent emissions norms. During the year 1990, biofuel production has started in several European countries and flourished in a meaningful way. In 2003, the European Union (EU) has set a target of the contribution of biofuels to 5.75% of its energy consumption by 2010 and 20% in 2020. France has adopted the EU target and has set more ambitious goals, in 2008 biofuels have represented 5.75% of its energy consumption and it tries to reach 10% in 2015, making an advance of 2 years on European targets (Bozbas 2008). Biodiesel is one of the most available sources of renewable energy, it is non-toxic, biodegradable, its heating value is high, it has zero sulfur content and its use in diesel engines reduces the emissions (Dalvi and Chandrakant 2012; Ayhan 2007; Capareda, Powell and Parnell 2008; Senthil Kumar, Ramesh and Nagalingam 2010). It can be used directly in diesel engine without introducing any changes. However, there are technical problems related to its flow properties at lower temperatures, the emissions of NO_x and stability during storage (Bandel and Heinrich 1982; Kalam and Masjuki 2004; Vedaraman et al. 2011). The most important problem for the moment is high production cost of which raw materials accounts 60–85% of the total price of production. Using waste fats instead of edible oils as raw material for biodiesel production may resolve that problem (Meng, Chen, and Wang 2008; Bai, Wang, and Tu 2009).

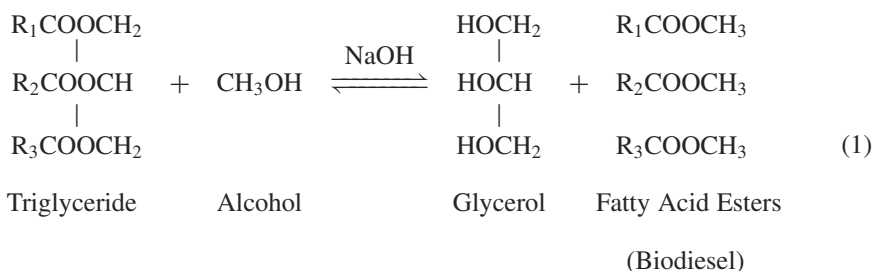
In this respect, fermentation, transesterification, and pyrolysis of biomass, industrial, and domestic wastes have been proposed during the last years as an alternative solutions for biofuel production (Luo et al. 2004; Leung, Wu, and Leung 2010). A number of methods are currently available and have been adopted for the biodiesel production, among which there are three primary methods are described in the literature: alkali-catalyzed, acid-catalyzed, and enzyme-catalyzed transesterification. Due to the process cost, alkali-catalyzed transesterification seems to be the most commonly adopted method (Antolín et al. 2002; Berchmans and Hirata 2008; Leduc et al. 2009).

On the whole, during these processes several variables (i.e., reaction temperature and reaction time) affect the ability of triglycerides to react and the yield of biodiesel production. The highest yield of biodiesel can be obtained under the optimal conditions, which are sensible, different in function of the raw material nature and chemical structure. As a consequence, the work presented in this article focused on the identification of these optimal conditions in the case of using three types of waste oils as raw materials for biodiesel production by alkali catalyzed transesterification process.

EXPERIMENTAL SETUP

Basic Chemical aspects of Transesterification Process

Transesterification is a chemical reaction that consists on substituting alcohol groups of an ester by another type of alcohol which is given in Eq. (1). This process is widely used to reduce the viscosity of triglycerides, which limits their direct use in diesel engines. Transesterification is a reversible reaction, which consists of mixing the reagents. The presence of a catalyst greatly promotes this reaction and reduces considerably the reaction time.



Several processes have been developed for biodiesel production, either by catalysis: acidic, basic, and enzymatic, in homogeneous or heterogeneous systems, either by methods that operate without a catalyst at very high temperatures and pressures. The reaction following an alkali catalyst is the most widespread in the industrial field, for its low output price and triglyceride conversion rate. The problem of this method is related to the sensitivity of the response to moisture and the free fatty acids (FFAs) levels, which form soaps in the presence of a strong base (Jeong, Yang, and Park 2009).

Raw Materials

In the present study, the WCO was collected from the restaurant of Ecole des Mines de Nantes. Based on their acid values, three types have been identified: WCO1, WCO2, and low acidity waste cooking oil (WCOLA). Its composition was described on the products wrapping. And it was as follows: 45% palm oil, 45% sunflower oil of which 35% are enriched with oleic acid, and 10% of rapeseed oil. WCO1 and WCOLA were used to make French fries and WCO2 which was used to cook meat and fishes. The physical-chemical characteristics of these WCOs are described in Table 1.

Transesterification Process of WCOs

Initially, NaOH was mixed with the alcohol (methanol—CH₃OH or ethanol—C₂H₅OH). Then, the mixture was stirred by means of a magnetic stirrer under constant temperature (30°C) for 5–10 min, until any traces of solid NaOH are not observed, which means that the reaction is accomplished. The purpose of premixing alcohol with NaOH is to produce alkoxide, which reacts more effectively with the triglycerides. Then the WCO and alkoxide were mixed together under continuous and vigorous stirring at different temperatures and for different times that will be specified later in this article. At the end of

Table 1 Physical-Chemical Characteristics of WCOs

WCO type	Acid value (mgKOH/g)	Moisture (%)	Viscosities at 40°C		High heating value, (HHV) (MJ/kg)	Melting point (°C)	Density (g/cm ³)
			Dynamic (mPa·s)	Kinematic (mm ² /s)			
WCOLA	0.8	<0.05	32.9	37.8	40	30	0.87
WCO1	1.4	<0.05	33.1	38.0	40	30	0.87
WCO2	6.5	<0.05	33.0	37.9	40	30	0.87

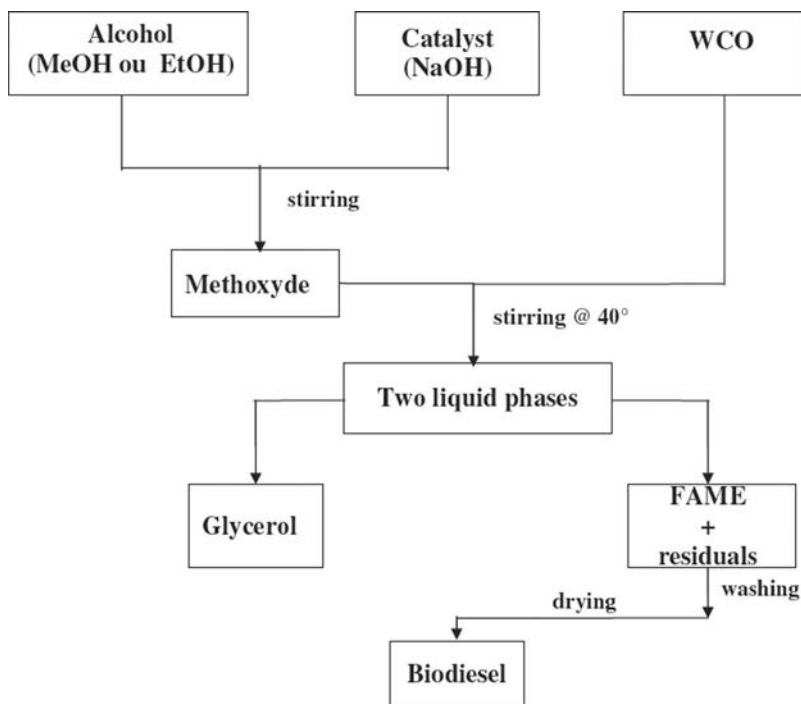


Figure 1 Flow Chart of Transesterification Process.

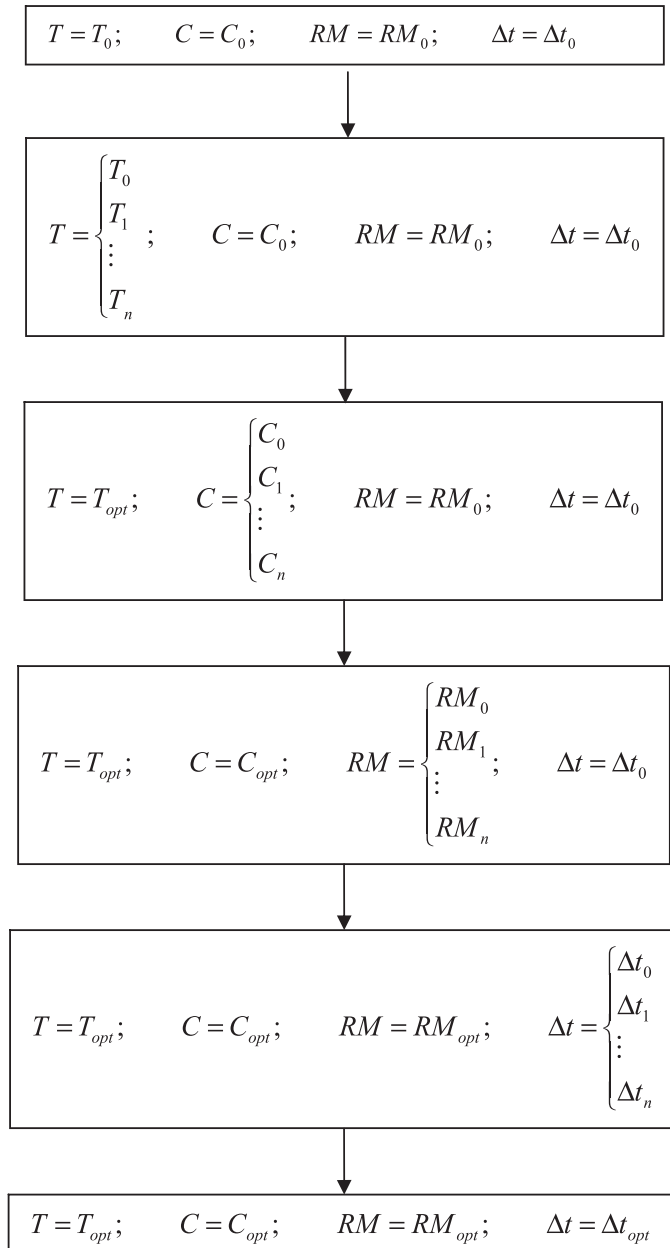
reaction, the products were poured on a separating funnel in order to separate the glycerol phase from biodiesel.

As both phases contain alcohol and catalyst, after the separation step, the biodiesel was washed several times with water, until the aqueous phase became clear and neutral. Product drying is ensured by using anhydrous calcium chloride, and after that the biodiesel is filtered and weighed. The flow chart of transesterification process is given in Figure 1. Considering Eq. (1), the yield of biodiesel was calculated as the percentage of the weighed product from the expected weight, calculated as theoretical conversion. At the end of these operations, the physical-chemical characteristics of the produced biodiesel were studied.

The main factors affecting the alkali-catalyzed transesterification are:

- Alcohol quantity
- Reaction temperature
- Reaction time
- Catalyst concentration

The aim of this study is to obtain the maximum yield of biodiesel by searching the optimal combination of the listed parameters. In order to study a higher number of parameters with a larger range of values, the effects of interaction were not taken into consideration. The optimization was done by optimizing each parameter and then the optimal condition was determined which is shown in Figure 2.



Symbols :	subscript :
T = temperature	0 = initial values
C = catalyst amount	Opt = optimal value
RM = oil:alcohol molar ratio	
Δt = reaction duration	

Figure 2 Flow Chart for Optimisation of Reactions.

RESULTS AND DISCUSSION

Transesterification of WCO1

Transesterification with Methanol (CH₃OH). The most common transesterification process uses methanol to produce methyl esters (commonly referred to as fatty acid methyl esters–FAME) as it is the cheapest alcohol available. Initially, transesterification process was realized at different reaction temperatures: 30, 40, 45, 50, and 60°C with three different molar ratios of 1:6, 1:9, and 1:12 and with three reaction times of 30, 45, and 60 min. The effect of catalyst quantity was identified by using five concentrations: 0.5%, 0.6%, 0.8%, 1%, and 1.25% which is calculated from total oil weight of WCO.

Based on literature information (May 2004; Phan and Phan 2008; Jeong, Yang, and Park 2009), the study started with the following combination of process parameters: reaction temperature: 60°C, oil to alcohol ratio: 1:6, catalyst amount: 1%, and reaction time: 60 min; at 60°C (the temperature recommended by literature because it is near to the boiling point of methanol). At temperatures higher or equal to 50°C, gel and soap formation occurred without any phase separation. At 45°C and 40°C the conversion reached 75% and 79.2%, respectively, while, at 30°C, no phase separation was detected. As a consequence, the temperature of 40°C was adopted as optimal value for this type of WCO. Table 2 illustrates the optimization scheme followed for WCO1 with methanol.

Transesterification with Ethanol (C₂H₅OH). Ethanol can be used to produce an ethyl ester, commonly referred to as fatty acid ethyl ester (FAEE). The same approach that was used with methanol is used with the substituting the methanol with ethanol. In the case of using WCO1, the optimal values of temperature and catalyst amount have remained the same, but, the oil to alcohol ratio has been changed. For a ratio of 1:6 the reaction did not occur, for a ratio of 1:9 the yield reached 76.3%, and with 1:12 the yield decreased to 75.9%. And the reaction time required was 60 min. Table 3 illustrates the optimization scheme followed for WCO1 with ethanol.

Table 2 Optimization of WCO1 Transesterification with Methanol

Temperature (°C)					Catalyst amount (%)					Molar ratio			Δt (mn)			η (%)	
30	40	45	50	60	0,5	0,6	0,8	1	1,25	1:6	1:9	1:12	30	45	60		
X								X		X						X	–
	X							X		X						X	79,2
		X						X		X						X	75
			X					X		X						X	–
				X				X		X						X	–
	X				X					X						X	50
	X					X				X						X	54
	X						X			X						X	60
	X							X		X						X	79,2
	X								X	X						X	77
	X							X		X							79,2
	X							X			X						80
	X							X				X					82
	X							X		X			X				–
	X							X		X				X			79
	X							X		X					X		79,2

Table 3 Optimization of WCO1 Transesterification with Ethanol

Temperature (°C)			Catalyst amount (%)			Molar ratio			Δt (mn)			η (%)
40	45	50	0,8	1	1,25	1:6	1:9	1:12	45	60	120	
X				X			X				X	75,9
	X			X			X				X	72,3
		X		X			X				X	–
X			X				X				X	54
X				X			X				X	75,9
X					X		X				X	65,5
X				X		X					X	–
X				X			X				X	75,9
X				X				X			X	69
X				X			X		X			–
X				X			X			X		76,3
X				X			X				X	75,9

Transesterification of WCO2

Transesterification with Methanol (CH₃OH). In order to establish the optimal conditions for WCO2, the same approach as for WCO1 has been used. With the same optimal conditions as that of WCO1, the transesterification of WCO2 has not occurred. It is known that the high FFA content will react with catalyst and neutralize it. By increasing the amount of catalyst, this problem could be overcome. Several amounts of catalyst were tried: 1.25%, 1.5%, and 2%. The optimum yield occurred between 1.25% and 1.5% of catalyst amount. Using 2% NaOH, the soap formed during the reaction resulted on a gel and froze the biodiesel production. Thus, the value of 1.25 was fixed as an optimal catalyst amount. In order to optimize the oil to alcohol molar ratio, the following values were used: 1:6, 1:7.5, and 1:9. The maximum biodiesel yield was obtained for a molar ratio of 1:7.5. For superior oil to methanol ratios, lower yields were obtained because of the tendency of FAMES to make emulsions with glycerol in the presence of higher amounts of alcohol, and thus a very difficult phase separation occurs at the end of process. The study on the effect of reaction temperature and time variation indicates that the best biodiesel yield is obtained at 45°C and 45 min. The detailed optimization process is shown in Table 4.

Transesterification with Ethanol (C₂H₅OH). The WCO2 transesterification using ethanol failed after several experiments, in all tests gels were obtained and any phase separation was not observed. So, it is concluded that the production of ethyl esters is more sensitive to oil acidity than that of methyl esters.

Transesterification of WCOLA

The WCOLA samples were obtained in a later period of this study, after the optimization of the reaction with the WCO1 and WCO2. In order to evaluate the effect of increasing or decreasing the acid value of the raw material, the optimization of the reaction with the latest sample was planned. Since its acid value was nearest to WCO1, the optimization started with the optimal values obtained in Tables 2 and 3, the yield reached 97% and 95% with methanol and ethanol, respectively. So the need of optimization was not justified with these reaction efficiencies, and the optimal parameters were set like those of

Table 4 Optimization of WCO2 Transesterification with Methanol

Catalyst amount (%)				Temperature (°C)			Molar ratio			Time (min)		η (%)
1	1,25	1,5	2	40	45	50	1:6	1:7,5	1:9	45	60	
X				X			X				X	–
	X			X			X				X	75,7
		X		X			X				X	69,4
			X	X			X				X	56,4
	X			X			X				X	75,7
	X				X		X				X	72,5
	X					X	X				X	–
	X			X			X				X	75,7
	X			X				X			X	71,7
	X			X					X		X	71
	X			X			X			X	X	75,3
	X			X			X				X	75,7

Table 5 Optimal Reaction Conditions for Different WCOs and Alcohols

WCO	Alcohol type	Acid value (mgKOH/g _{oil})	Molar ratio (oil:alcohol)	Temperature (°C)	Catalyst amount [%]*	Temps (min)	η (%)
WCOLA	Methanol	0,8	1:6	40	1	45	97
WCOLA	Ethanol	0,8	1:9	40	1	60	95
WCO1	Methanol	1,4	1:6	40	1	45	80
WCO1	Ethanol	1,4	1:9	40	1	60	73
WCO2	Methanol	6,5	1:6	40	1,25	45	76

*Based on WCO mass.

WCO1. The WCOLA can be considered as a reference raw material for these experiences, because its acid value is very close to those of pure vegetable oil. The established optimum conditions for the applied process are listed in Table 5.

Effects of Different Reaction Parameters on the Transesterification Process

Effect of alcohol quantity on the transesterification of WCOs.

Theoretically, as the reaction stoichiometry shows, transesterification reaction requires 3 mol of alcohol for 1 mol of triglycerides to produce 3 mol of fatty acid ester and 1 mol of glycerol [refer Eq. (1)]. As a reversible reaction, an excess of alcohol is needed to shift the equilibrium toward the biodiesel production to ensure that triglycerides will be completely converted to esters. Although its positive effect on the transesterification reaction, increasing the excess of alcohol, enhances the formation of emulsions of biodiesel in glycerol phase which decreases the recovered fuel. In this work, this problem appeared more likely when ethanol is used, and that may explain the lower yields of ethyl esters and, on the other hand, the loss in recovered biodiesel.

The catalyst will form soap with FFAs and, in this environment, the produced esters seem to exhibit more tendencies to form gels. Moreover, it is known that soaps are good emulsifiers and they create proper conditions for the reaction mixture to become a stable emulsion. In this case, the esters remain captured in the emulsion and at the end of process

no separation phase was formed. Considering these effects, there is a reduction of biodiesel yield while the acid value of WCO increases. At the same time, comparing with results obtained during the transesterification with methanol, ethanol shows a clear tendency to produce lower amounts of biodiesel with WCO1 and WCOLA, and the formation of gel and soaps in reaction with WCO2.

Effect of reaction time on the transesterification of WCOs. In transesterification, conversion rate increases with reaction time until the optimum value. In the applied alkali-catalyzed transesterification, the process begins with the mixing and dispersion of sodium alkoxide (methoxide and ethoxyde in the present study) molecules into the oil. The conversion rate is relatively low for this step of the process and due to oil–alcohol immiscibility the mixture has a milky aspect. After 10–15 min, the mixture becomes clear and the reaction proceeds relatively fast. An excessively reaction time led to a reduction in biodiesel yield as a consequence of backward reaction resulting in more FFAs, more susceptible under the applied conditions to form soap than organic esters.

Effect of reaction temperature on the transesterification of WCOs. The present study shows that the temperature has an essential effect on the reaction rate and the biodiesel yield. Increasing temperature accelerates the reaction and increases the yield of biodiesel (May 2004; Meher, Sagar, and Naik 2006; Phan and Phan 2008; Jeong, Yang, and Park 2009), which is quit logical, as a higher reaction temperature results in a decreasing oil viscosity so that a more effective contact between triglycerides and alkoxide molecules. But on the other hand, it promotes parallel reactions, especially saponification, which could play an inhibitor role for transesterification (Meng, Chen, and Wang 2008; Phan and Phan 2008; Jeong, Yang, and Park 2009). Van Gerpen et al (Van Gerpen, Shanks, Pruszko, Clements and Knothe 2004) suggests that the temperature of 40°C in order to avoid saponification.

In this study, the results were congruent more with *Dreger's* (Dreger 1945) observations. That comes probably from the fact that the WCO has a higher acidity than pure oils, contains impurities and it was subject of thermal treatment which may be affected its chemical structure.

Effect of catalyst concentration on the transesterification of WCOs. It was established that the catalyst amount has an important influence on both reaction conversion and biodiesel yield. Without catalyst, the reaction does not occur unless using the supercritical alcohol method which requires high temperatures and pressures. In the case of using an alkali-catalyst, increasing the catalyst's amount accelerates the reaction but beyond a certain value the NaOH will react with fatty acids and the saponification will be favored (Ma and Hanna 1999; Lin et al. 2009).

Comparison of Physical-Chemical Characteristics of Biodiesel Derived from WCOs

The produced biodiesel was subjected to several tests to determine its physical and chemical characteristics. The results are presented in Table 6 and the variation of kinematics viscosity with temperature is plotted in Figure 3.

The viscosity was measured by using a vibro-viscosimeter SV-10 made by A&D Company. Dynamic viscosities of ethyl and methyl esters were measured between 25°C and 60°C. The acid values were measured by the volumetric titrimetry method. For all biodiesel samples, the identified values were lower than 0.2 mg KOH/g. Water content was determined by using xylene vapors method and there is no water is present in the biodiesel.

Table 6 Physical-Chemical Characteristics of Produced Biodiesels

Characteristic	Units	EELA	MELA	ME1	EE1	ME2
Density	g/cm ³	0.868	0.869	0.870	0.868	0.870
Carbon content	w/w	76.57	76.60	75.96	77.23	76.7
Hydrogen content	w/w	12.96	12.85	13.04	12.8	12.7
Oxygen content	w/w	10.47	10.55	11	9.97	10.6
Higher heating value	MJ/kg	40.13	40.05	39.92	40.24	39.98
Lower heating value	MJ/kg	37.51	37.43	37.29	37.61	37.17
Kinematic viscosity @ 40°C	mm ² /s	3.88	3.73	3.61	3.95	3.7
Flash point	°C	158	160	162	160	158
Water content	mg/kg	–	–	–	–	–
Acid value	mgKOH/g	–	0.08	0.07	0.12	0.1
Sulfur content	mg/kg	–	–	–	–	–

Abbreviations: EELA, ethyl ester of low acid value waste cooking oil;

MELA, methyl ester of low acid value waste cooking oil;

ME1, methyl ester of waste cooking oil 1;

EE1, ethyl ester of waste cooking oil 1;

ME2, methyl ester of waste cooking oil 2.

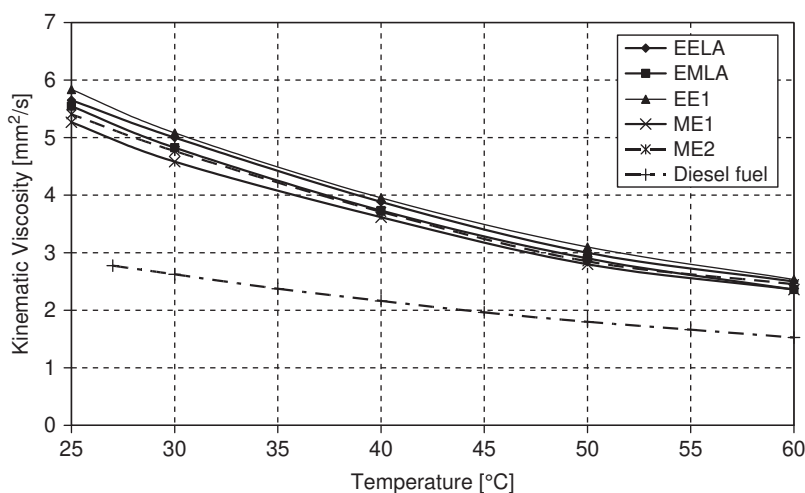


Figure 3 Evolutions of Kinematic viscosities of biodiesel wit temperature (ME – methyl ester, EE – ethyl ester. “1” shows that the ester is prepared by WCO1 transesterification, “2” is corresponding to WCO2 and “LA” to WCOLA).

The elemental analysis was conducted using a CHNS-O Analyzer FLASH 1112 series E.A and the biodiesel has the following composition: 76.59% C, 12.91% H, 0% S, 0% N, and 10.5% O. The molar composition is derived from the formula by dividing the mass composition of each element by its molar mass, thus 100 g of biofuel contains: 6.3825 mol of C, 12.91 mol of H, and 0.65625 mol of O. Finally, dividing the molar composition by 0.65625 (the molar contenance of Oxygen). It is concluded that the empirical formula of the biodiesel is C_{9,72} H_{19,66} O. This empirical formula will be used in the study of combustion of this biofuel in internal combustion engines. The higher heating value was measured

Table 7 Methyl Esters Compositions of Biodiesel Produced from the Different WCO

	WCOLA	WCO1	WCO2
Myristic acid methyl ester	0,90	0,94	0,99
Palmitoleic acid methyl ester	0,25	0,15	0,82
palmitic acid methyl ester	41,00	39,00	33,88
Stearic acid methyl ester	12,20	13,10	16,85
Oleic acid methyl ester	42,70	43,10	40,58
Linoleic acid methyl ester	2,15	2,33	2,99
Methanol	Traces	Traces	Traces
Glycerol	Traces	Traces	Traces
Total	99,20	98,60	96,13

Table 8 Characteristics of Biodiesel Compared to European Norm EN 14214

Characteristics	Units	EN 14214 limits		Produced biodiesel
		Min	Max	
Density	g/cm ³	0.86	0.90	0.87
Kinematic viscosity	mm ² /s	3.50	5.00	3.61–3.95
Flash point	°C	110	–	158–162
Water content	mg/kg	–	500	0
Acid value	mgKOH/g	–	0.50	0.08–0.12
Sulfur content	mg/kg	–	10	0
Esters	%	96.5	–	98
Methanol	%	–	0.2	Traces (ppm)
Glycerol	%	–	0.02	Traces (ppm)

with an isoperibolic PARR 6200CLEF calorimeter. The flash point was measured with a PENSKEY MARTENS NPM440 apparatus.

The amounts of FAME/FAEE, glycerol, and alcohol were measured by using the gas chromatography analysis. In this purpose, a Perkin Elmer “Clarus 500 Gas Chromatograph,” equipped with a flame ionization detector and a capillary column (VARIAN WCOT Fused Silica, 30 m × 39 μm × 25 μm) was used. The mentioned compounds were identified by comparing their retention time to the retention time of standard compounds. The results of the Chromatographic Analysis are listed in Table 7. The properties of biodiesel compared with diesel and European norms are given in Table 8.

CONCLUSIONS

In this work, biodiesel was derived from various WCOs by alkali-catalyzed transesterification reaction, using two types of alcohol, methanol, and ethanol. Also the optimal conditions for these reactions were determined, depending on acidity of WCO and alcohol types. The effects of the following process variables were investigated: reaction temperature, catalyst amount, type of alcohol, reaction time, and WCO acidity. Based on the present work, the following conclusions are drawn:

- The high-quality biodiesel was successfully derived from WCOs by alkali-catalyzed transesterification.

- The measured physical and chemical properties of produced biodiesel were almost the same, and independent of raw materials acidity. Moreover, slight differences between ethyl esters and methyl esters have been obtained.
- The lower heating value of the biodiesel is a little lower than that of diesel oil, which will increase the fuel consumption of the engine for the same power output.
- It is concluded that the FFA content has a negative effect on the whole process. The FFAs form soap with the catalyst, which reduce considerably its efficiency for transesterification. Thus higher amounts of catalyst are required. The formation of soap during alkali-catalyzed reaction creates proper conditions for emulsions appearance; so that, the esters are captured into a stable emulsion with glycerol and excess alcohol and at the end of process the phase's separation will not be possible.

Based on this work, it is recommended to use methanol in alkali-catalyzed transesterification of waste oils with relatively high FFA contents. To avoid their negative effects, FFAs in the base oil are either converted to soap, and removed from the process, or they may be esterified (yielding more biodiesel) using an acidic catalyst.

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