TRANSPORT
ISSN 1648-4142 print / ISSN 1648-3480 online
2013 Volume 28(3): 276–289
doi:10.3846/16484142.2013.830644

BIODIESEL PRODUCTION FROM WASTE FRYING OIL AND ITS APPLICATION TO A DIESEL ENGINE

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Submitted 7 September 2011; accepted 17 November 2011

Abstract. A transesterification reaction of Waste Frying Oil (WFO) with methanol in the presence of a sodium hydroxide catalyst was performed by means of two different methods: a one-step and a two-step. The effects of NaOH concentration and the molar ratio of methanol to WFO on the conversion of WFO to biodiesel were investigated and optimized for both methods. The results showed that, for one-step method, the optimal parameters for maximum biodiesel yields were found to be methanol to WFO molar ratio of 5:1, catalyst concentration of 0.7 wt% of WFO, reaction temperature of 50°C, reaction time of 1 h and stirring speed of 200 rpm, whereas the maximum biodiesel yield reached 95%. While, for the two-step method, the optimal parameters were 3.5:1 and 0.49 wt% of WFO for the first step, and 1.5:1 and 0.21wt% of WFO for the second step, whereas the maximum biodiesel yield reached 88.3% and 96.4%, respectively. Other parameters were the same as for one-step method. The two-step method enhances the yields of biodiesel by about of 2% as compared with the one-step method. In addition, the properties of WFO, the produced biodiesel and the diesel fuel were characterized by the Fatty Acid (FA) content (except diesel fuel), using Gas Chromatography (GC) analysis, and the density, viscosity, flash point, cloud point, carbon residue, and the acid value according to ASTM D6751-12 standard. While the Cetane Number (CN), lower heating value, stoichiometric Air Fuel Ratio (AFR) and iodine value were calculated based on FA composition, the results of GC analysis showed that, the FA composition of the WFO and its methyl esters was not changed with transesterification. Palmitic (C16:0), Stearic (C18:0) and Palmitoleic (C16:1) and Oleic (C18:l) acids were the most common saturated and monounsaturated FAs, respectively. Similarly, Linoleic (C18:2) and Linolenic (C18:3) were the most common polyunsaturated FAs. The physical and chemical properties results showed that the biodiesel density, viscosity and acid value were lower than of WFO and higher than diesel fuel. Also, the molecular weight, the CN, the flash point and the carbon residue of the biodiesel were higher, and the lower heating value and the stoichiometric AFR were lower than those of diesel fuel. However, all biodiesel properties met the ASTM D6751-12 or EN 14214:2008 standards. Additionally, an experimental study was conducted to evaluate the effects of produced biodiesel and its blends with diesel fuel on a diesel engine performance in comparison with diesel fuel. The results showed that, when the engine operates on pure biodiesel and on a fuel blend, the brake power and the brake specific fuel consumption were increased, while the brake thermal efficiency and the equivalence AFR were decreased. In consequence, the produced biodiesel can be used as a diesel fuel substitute from the point of view of their characteristics similarity.

Keywords: transesterification; waste frying oil; biodiesel; methanol; diesel engine performance.

Reference to this paper should be made as follows: Al-Hasan, M. I. 2013. Biodiesel production from waste frying oil and its application to a diesel engine, *Transport* 28(3): 276–289. http://dx.doi.org/10.3846/16484142.2013.830644

Introduction

The depletion of the world's petroleum reserves and the increasing energy demand and environmental concerns all over the world, drive the researchers to search for alternative sources of petroleum-based fuel, such as gasoline and diesel fuels. Recently, biodiesel has been considered as the best candidate for a diesel fuel substitution, because it can be used in any diesel engine without any modification. Biodiesel has been defined as mono alkyl ester (methyl or ethyl ester) of long chain (C16–C18) fatty acids derived from a renewable lipid feedstock, such as vegetable oils or animal fats ASTM D6751-12. The

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main advantages of using this alternative fuel are that it is renewable, non-inflammable, biodegradable and non-toxic. Moreover, it reduces most exhaust emissions, such as carbon monoxide, unburned hydrocarbons, sulfur dioxide and particulate matter except NO_x (Kaieda *et al.* 1999; Agarwal, Das 2000; Canakci *et al.* 2006). On the other hand, the main disadvantage of using biodiesel is the high cost of the raw materials, which leads to a very expensive final product in comparison with diesel fuel. Van Gerpen *et al.* (2006) and Van Gerpen (2005) reported that, 75÷80% of the production cost of biodiesel is the cost of the oil to produce a fuel that is competitive with diesel fuel and requires a low-cost feedstock. Therefore, research is being conducted for alternative ways to reduce the cost through the application of more-effective production technologies and the use of inexpensive vegetable oils for the production of Fatty Acid (FA) esters (De Oliveira *et al.* 2004). The use of Waste Frying Oil (WFO) instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost. Moreover, the use of waste frying oil for biodiesel production has additional benefits such as: treatment of a waste product and the provision of an efficient use of a resource. However, it is necessary to note that the WFOs have properties different from those of virgin oils. In this aspect, the high temperature of the frying processes and the water from the foods accelerate the hydrolysis of triglycerides, and increases the Free Fatty Acid (FFA) content in the oil. Also, the viscosity, density, saponification value and iodine value (IV) are different when virgin oils are used (Tomasevic, Siler-Marinkovic 2003).

The most common way to produce biodiesel is by transesterification, which involves stripping the glycerin from the FAs with a catalyst, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH), and replacing it with an anhydrous alcohol that is, methanol or ethanol to yield methyl, or ethyl esters and glycerol.

Theoretically, the stoichiometric transesterification reaction requires 3 mol of methanol (or ethanol) and 1 mol of triglyceride to give 3 mol of FA methyl (or ethyl) ester and 1 mol of glycerol. However, in order to increase the yields of the alkyl esters and to allow its phase separation from the glycerol to be formed, an excess of the alcohol is used to shift the equilibrium to the product side (Ma, Hanna 1999; Schuchardt *et al.* 1998). Currently, transesterification reactions have been studied for many vegetable oils such as: soybean, rapeseed, sunflower, safflower, canola and palm oil. Since the prices of edible vegetable oils, for example, soybean oil, are higher than of diesel fuel, waste and non-edible vegetable oils have been investigated as potential low priced biodiesel sources.

The production of biodiesel that originates from WFO has been the subject of several researches and commercial applications throughout the world. Çetinkaya and Karaosmanoğlu (2004) have studied the optimum conditions and the refining procedures for biodiesel production from restaurant-originated used cooking oil. As a result, three alternative reaction conditions were obtained for pilot-scale and industrial scale biodiesel production purposes that is (1:6, 1, 60), (1:5, 2, 120) and (1:6, 2, 30) oil/alcohol molar ratio, sodium methodize amount (% by the weight of the oil); and reaction time (min.), respectively. Dorado *et al.* (2004) investigated and optimized the chemical parameters involved in waste olive oil transesterification. Their study showed that, fuel specifications were close to those of diesel fuel, thus indicating that methyl esters from used olive oil can be considered as a fuel candidate. Haas (2005) investigated the production of methyl ester from soap stock, a by-product of edible oil, using acid-catalyzed esterification method. He found that the FA composition of the resulting ester was largely similar to that of soybean oil and met the established specifications for biodiesel of the ASTM D6751-12 standard. Zheng *et al.* (2006) studied the optimum process parameters and reaction kinetics in the acid catalyzed transesterification of WFOs, where they reported that the oil-methanol-acid molar ratios and the temperature were the most significant factors affecting the yield of Fatty Acid Methyl ester (FAME). Georgogianni *et al.* (2007) studied the transesterification of two different frying oils (soybean oil and a mixture of soybean and cotton seed oil) with methanol and NaOH as a catalyst, by means of low-frequency ultrasonication (24 kHz, 200W) and mechanical stirring (600 rpm) for the production of biodiesel fuel. The two different frying oils gave similar yields of isolated methyl esters under both mechanical stirring and ultrasonication. Chhetri *et al.* (2008) and Meng *et al.* (2008) used NaOH as the catalyst in the transesterification of WFO and reported that 0.8% and 1% (w/w of oil) NaOH are the optimum catalyst concentrations, respectively. A. N. Phan and T. M. Phan (2008) studied the effects of methanol/waste cooking oils ratio, KOH concentration and reaction temperature on the biodiesel conversion. As the result, the biodiesel yield was 88÷90% at the methanol/oil ratios of 7:1÷8:1, temperatures of 30÷50 °C and 0.75 wt% KOH. Dorado *et al.* (2002) studied the two-step transesterification reaction of waste oils from Brazil, Spain and Germany. Stoichiometric amounts of methanol and the necessary amounts of KOH, supplemented with the exact amount of KOH to neutralize acidity, were used during the experiments. Both reactions were completed in 30 min. The temperature range was 40÷60 °C. Parameters such as density, viscosity, water content and energy content were investigated. It was concluded that a two-step, alkaline-catalyzed transesterification reaction is an economic method for biodiesel production used from vegetable oil. Issariyakul *et al.* (2007) investigated the transesterification of waste fryer grease containing 5÷6 wt%

FFA with methanol, ethanol, and mixtures of methanol/ethanol maintaining the oil to alcohol molar ratio of 1:6, and initially with KOH as a catalyst used two-step (acid and alkali catalyzed) method for biodiesel synthesis. They found that more than 90% ester can be obtained when two-step method was used, compared to 50% ester in single-step alkaline catalyst. Encinar *et al.* (2007) studied the transesterification reaction of WFO by means of ethanol, using sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide as catalysts, and found that the biodiesel with the best properties was obtained using an ethanol/oil molar ratio of 12:1, potassium hydroxide as catalyst (1%), and 78 °C temperature. In addition, they showed that the two-step transesterification of WFO was better than the one-step process, and the yields of ethyl esters were improved 30% in relation to the one-step transesterification. Çaylı and Küsefoğlu (2008) also have reported the results of comparing one-step and two-step base-catalyzed room temperature transesterification reaction of used cooking oil. In the two-step, for each 1000 g of used cooking oil, 4.2 g NaOH and 140 ml methanol were used in the first step, and 1.8 g NaOH and 60 ml methanol were used in the second step. The effects of water content and suspended particles on the yield were studied. It was found that the two-step process gives a better yield than the one-step process. Wan Omar *et al.* (2009) optimized the pre-treatment step of a two-step biodiesel production from waste cooking oil. Pre-treatment with ferric sulphate in acid-catalyzed esterification process preceded transesterification in order to reduce the FFA level in the waste cooking oil. The authors investigated the relationship between reaction temperature, reaction time and methanol to oil molar ratio in the pre-treatment step. The best operating conditions for the pre-treatment step were found to be 60 °C, 3 h and 7:1 for the reaction temperature, reaction time and methanol to oil molar ratio respectively, with 81.3% FAME yield. The above literature review indicates that the optimum conditions for biodiesel production are not compatible. They strongly depend on the used feedstock. Additionally, there are a few references, which give detailed information for two-step base catalyzed transesterification method. Therefore, the aim of this work was to optimize the conditions of biodiesel production from Jordanian waste frying oil as a raw material in the transesterification process by using one-step and two-step base catalyzed methods, as well as to evaluate the produced biodiesel as a fuel in a diesel engine.

1. Experimental details for biodiesel production

1.1. Materials

Jordan is a large vegetable oil consumer, mainly olive, palm and sunflower oils. These oils are largely used for deep frying processes. Consequently, thousands of litres of WFO can be collected annually, because most household waste frying oil is discarded through the drainage system. Hence, a substantial amount of biodiesel fuel can be prepared from these wastes, which would be partly reducing Jordan's dependency on diesel fuel.

This research was carried out in Al-Balqa Applied University in Jordan during the year 2011. For the purpose of this study, samples of WFO of edible vegetable oils were used in the experiments. WFOs were collected from different domestic sources, blended together in order to obtain mixture of different WFOs. The collected oils were first filtered to remove food residues and solid precipitate in them, and heated up to about 110 °C for 10 minutes to remove all water present in the oil. It was again filtered and stored in a container as feedstock for experimental use. The reagents used for transesterification process were: methanol 99% (Assay, UK) and sodium hydroxide 99% (Assay, UK).

1.2. Methods and equipments

The equipments used for transesterification were: a 500 ml cylindrical graduated glass vessel, digital thermometer with accuracy of ±1%, a magnetic stirrer hotplate provided with a temperature and stirring speed controllers (Stuart Scientific, UK) and Sartorius electronic balance scale – 2355 (readability of 0.1% g). The operation variables employed were methanol/WFO Molar Ratio (MR) (3:1, 4:1, 5:1, 6:1 and 7:1) and NaOH concentration (0.45, 0.50, 0.60, 0.70, 0.75 and 1.0) wt% of WFO. While WFO volume (200 ml), reaction time (60 min), reaction temperature (50 °C) and a stirring speed (200 rpm) were fixed as common parameters in all experiments. The transesterification procedure was as follows: the vessel was preheated to 70 °C, to eliminate moisture, and then 200 ml of WFO was added. The amounts of NaOH and methanol were measured and placed in the flask and stirred until the NaOH was completely dissolved. With the oils stirred and heated to a temperature of 58 °C (after pouring the NaOH and methanol solution to the WFO, the temperature of the reactants dropped to 50 °C) on a hot plate stirrer, the solution of NaOH and methanol was poured to the vessel, taking this moment as time zero of the reaction After one hour, the mixture was transferred to a separating funnel and allowed to separate overnight to produce two dissimilar layers that is, fatty acid methyl ester (biodiesel) and glycerol. After separation of the two layers by sedimentation, the biodiesel was purified by distilling the residual methanol and water at 110 °C. The remaining catalyst was extracted by successive washing with warm distilled water (50 °C) until the wash water became clear. Finally, the water present was removed by heating at 110 °C and the final product, biodiesel, was be obtained as a clear, light yellow liquid. After that the product yield was weighted for further analyses. The biodiesel production steps are shown in Fig. 1.

1.3. Transesterification

The transesterification process in this study was carried out by using one-step and two-step methods. Since the WFO, used in this study, has a low acid value (0.95 mg KOH/g), the transesterification process was applied directly without a titration (Table 1).

In one-step method, the effect of MR and NaOH concentration on biodiesel yield was evaluated. Forty experiments were performed with different combinations of MR and NaOH concentration, while keeping the reaction temperature (50 °C), reaction time (60 minutes) and stirring speed (200 rpm) constant. The MR was varied from 3:1 to 7:1, and the NaOH concentration was varied from 0.45 to 1 wt% of WFO. Two runs were carried out for each combination of reactants and process conditions. The average of the results was presented in Fig. 2. After these experiments, combination of optimum values of MR and NaOH concentration were evaluated on the basis of maximum percentage yield.

The results from one-step method, as reference conditions, were used to conduct the transesterification process by using a two-step method, as well as to the different combinations of NaOH concentration and MR for each step. Therefore, 5:1 MR and 0.7 wt% of WFO, represented by 43 ml methanol and 1.3 g NaOH, respectively, were used for a two-step method. The procedures were as follows: the MR and the NaOH concentration were divided into different groups by percents for the first and second step, as shown in Table 2. In the first step, for instance, trial 5 (70%, 30%), the methanol amount of 30 ml was added to 0.91 g of NaOH and stirred until the NaOH was completely dissolved. Then 200 ml of WFO was added to the preheated vessel and the methanol/ NaOH solution was added to the WFO. This mixture was stirred for 30 min at 50 °C, and then poured into a separating funnel. After an hour, the separation process happened and the glycerol was removed from the bottom of the separating funnel. The product was purified by distilling the residual methanol and water at 110 °C. In the second step, 13 ml methanol and 0.39 g of NaOH was prepared, and stirred until the NaOH dissolved. This was then added to the yield product obtained from the first step, and was again stirred for 30 min. After that, the mixture was added to a separating funnel and allowed to separate overnight. After separation of the two layers, the biodiesel was purified by the same way as discussed previously.

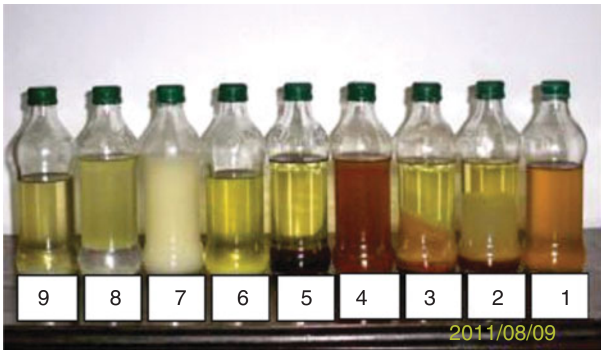

Fig. 1. Biodiesel production steps: 1 – WFO; 2, 3 – incomplete reactions; 4 – settling after transesterification process; 5 – two layers (FAME – upper layer and Glycerin – lower layer); 6 – FAME (biodiesel); 7 – water–FAME emulsion; 8 – separation process; 9 – FAME after separation from water

1.4. Analytical analyses

The biodiesel yields for one-step (B_1) and two-step (B_2) methods were estimated by using equations 1 and 2, respectively:

$$B_1 = \frac{m_{e1}}{m_o} \cdot 100\%; \tag{1}$$

$$B_2 = \frac{m_{e2}}{m_o} \cdot 100\%, \tag{2}$$

where: m_{e1} and m_{e2} are the masses of the produced biodiesel, after separation from glycerol, purified by distilling the residual methanol and water, washing with distilled warm water and finally purified by distilling the residual water, for one-step method and for the second step of the two-step method, respectively; m_o is the initial mass of the used WFO; m_p is the mass of the yield product from the first step of the two-step method (i.e. after being separated from glycerol and purified by distilling the residual methanol and water).

Fatty acid compositions of WFO and a produced biodiesel were determined by Gas Chromatography (GC) model 2010 (Shimadzu Corporation, Japan) equipped with a split injector, auto injector AOC–20i + s, a flame ionization detector (FID) and a DB–23 (60 m length, 0.25 mm I.D., 0.15 um film thickness) column with maximum temperature of 260 °C. The operational conditions for GC were explained well by Al-Hassan and Al-Odat (2011).

Based on the fatty acid compositions, the average molecular weight (M_w), the elemental composition, the Lower Heating Value (LHV) (Artamonov *et al.* 1976), the lower heating value of the blends (LHV_b), the stoichiometric air to fuel ratio (AFR) (Heywood 1988), the Saponification Number (SN) and the IV (Kalayasiri *et al.* 1996) and the Cetane Number (CN) (Krisnangkura 1986) can be determined by using the following equations:

$$M_w = \sum M_{wi} \cdot \chi_i; \tag{3}$$

Table 1. Chemical and physical properties of the tested fuels

Fuel property	Test method ASTM D6751-12 standard	ASTM D6751-12 and (EN 14214:2008) standards limits	Tested fuels		
			Diesel	Biodiesel	WFO
Typical formula	NA	NA	$C_{12.35}H_{21.76}$	$C_{18.73}H_{36.75}O_{1.96}$	$C_{17.7}H_{33.95}O_{1.97}$
Molecular weight	–	–	170	292.8	278.7
Elemental composition, wt%:					
C	NA	NA	87.12	76.82	76.42
H	NA	NA	12.88	12.31	12.28
O	NA	NA	0	10.76	11.31
Density 20 °C, kg/m^3	D 4052-09	NA (860÷900)	846.6	886.8	923.1
Kinematics viscosity @ 40 °C, mm^2/s	D 445-11a	1.9÷6.0 (3.5÷5.0)	3.288	4.683	35.34
Cetane number	–	> 47 (> 51)	47	48.32	45.54
Flash point, °C	D 93-10	> 130 (> 120)	68	178	NA
Cloud point, °C	D 2500-09	–	+7	+7	NA
CCR 100%, % mass	D 189-06	< 0.05 (NA)	0.03	0.07	NA
Acid value, mg KOH/g	D 974-08	< 0.8 (<0.50)	0.06	0.14	0.95
Iodine value,	NA	NA (<120)	NA	117.7	123.98
Linolenic FAME, % mass	NA	NA (<12)	–	1.91	1.95
Lower heating value, MJ/kg	NA	NA	42.82	37.64	37.41
Stoichiometric AFR, wt/wt	NA	NA	14.44	12.69	12.51

Note: NA – not available.

$$LHV = 33.9 \cdot \mathrm{C} + 125.6 \cdot \mathrm{H} - 10.9 \cdot \left(\mathrm{O_y} - \mathrm{S}\right) - 2.512 \cdot (9 \cdot \mathrm{H} - \mathrm{W}); \qquad (4)$$

$$LHV_b = \frac{\sum (f_i \cdot \rho_i \cdot LHV_i)}{\sum (f_i \cdot \rho_i)}; \qquad (5)$$

$$\mathrm{C_aH_bO} + c \cdot (\mathrm{O_2} + 3.776 \cdot \mathrm{N_2}) = d \cdot \mathrm{CO_2} + e \cdot \mathrm{H_2O} + c \cdot (3.776 \cdot \mathrm{N_2}); \qquad (6)$$

$$SV = \sum \frac{560 \cdot \chi_i}{M_{wi}}; \qquad (7)$$

$$IV = \sum \frac{254 \cdot D \cdot \chi_i}{M_{wi}}; \qquad (8)$$

$$CN = 46.3 + \frac{5458}{SN} - 0.225 \cdot IV, \qquad (9)$$

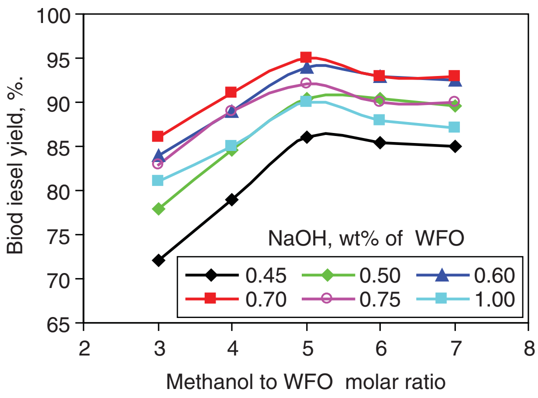

Fig. 2. The effect of NaOH concentrations on the biodiesel yield as a function of the methanol to oil molar ratios

Table 2. Experimental schedule for conducting a two-step method

Trial	First-step (Second-step)				
	Distributions, %	Methanol/WFO molar ratio	Methanol, ml/200 ml WFO	NaOH, wt%	NaOH, g/200 ml WFO
1	50 (50)	2.5:1 (2.5:1)	21.28 (21.28)	0.350 (0.350)	0.65 (0.65)
2	55 (45)	2.75:1 (2.25:1)	23.41 (19.16)	0.385 (0.315)	0.71 (0.58)
3	60 (40)	3:1 (2:1)	25.54 (17.03)	0.420 (0.280)	0.78 (0.52)
4	65 (35)	3.25:1 (1.75:1)	27.67 (14.90)	0.455 (0.245)	0.84 (0.45)
5	70 (30)	3.5:1 (1.5:1)	29.80 (12.77)	0.490 (0.210)	0.91 (0.39)
6	75 (25)	3.75:1 (1.25:1)	31.93 (10.64)	0.525 (0.175)	0.9 7(0.32)

where: M_{wi}, χ_i, D are the molecular weight, the percentage contribution and the number of double bonds of each FA component, respectively; C, H, O_y, S, W represent the elemental composition of fuels; f_i is the percentage contribution of the fuel in the blends; ρ_i is the fuel density (Tables 1 and 3).

Based upon equation 6, the molecular weights of oxygen, atmospheric nitrogen, atomic carbon and atomic hydrogen are 15.9994, 28.16, 12.011, and 1.008, respectively.

The chemical and physical properties of WFO and its methyl ester were determined according to the ASTM D6751-12 standard. These properties include density, viscosity, flash point, cloud point, carbon residue and acid value. In addition, the CN was determined based on the fatty acid compositions.

2. Results and discussion

The effects of the MR and the concentration of NaOH by using different biodiesel production methods on the conversion of WFO into methyl ester were studied. The FA composition, the physical and chemical properties of the WFO and its methyl ester were also determined.

2.1. One-step method

The effect of NaOH concentrations on the biodiesel yields for different MRs is shown in Fig. 2. As the Fig. 2 shows, the biodiesel yield increases with the increase of the NaOH concentration up to 0.7 wt% of WFO, which corresponds to the highest biodiesel yield, for all MRs.

However, further increase in the NaOH concentration beyond 0.70 wt% (e.g. 0.75% and 1%) leads to decrease of the biodiesel yield. The decrease in biodiesel yields can be attributed to the increase of glycerol and formation of fatty acid salts (soap). Thus, during transesterification process the following observations were observed: a small droplet of water on the vessel wall appears first, and then formation of soap (saponification), with the increase of NaOH concentration in the mixture. After that time and through a short period, the mixture turned to a viscous emulsion and thereafter to gel as shown in Fig. 1 (positions 2, 3). Also, it is well known that, soap formation consumes NaOH and this reduces its efficiency as a catalyst. The overall impact of these factors makes recovery of the methyl esters difficult and reduces biodiesel yield.

Also, it is obvious from Fig. 2 that, the MR increases beyond 5:1 (e.g. 6:1 and 7:1), leads to a decrease of biodiesel yield due to the increase of the NaOH concentrations, as well as to a dilution effect. Furthermore, the biodiesel yield decreases as the MR decreases to the levels below 5:1 (e.g. 3:1 and 4:1). According to the above results, the best operating conditions for one-step transesterification method were found to be 0.7% of NaOH concentration and 5:1 MR, with biodiesel yield of 95%. This can be attributed to the maximum ester conversion by the adequate concentration of NaOH and the amount of the MR in the reactants.

2.2. Two-step method

The optimum values of MR and the NaOH concentration obtained from a one-step method were adopted to conduct the first-step and the second-step of a two-step method.

The effect of MR with different NaOH concentrations were studied as presented in Fig. 3a and Fig. 3b for the first-step and the second-step, respectively. From Fig. 3a, it can be observed that, the biodiesel yield increases with the increase of both the MR and the NaOH concentrations. While from Fig. 3b the biodiesel yield increases with the increase of the MR and NaOH concentration until 1.5:1 and 0.21 wt%, respectively and then decreases. However, the biodiesel yield that is obtained from the second-step is higher than the first-step, as indicated on Fig. 3b. This increase can be attributed to the fact that, the materials that is, FAME, which were used for the second step have a low viscosity due to the transesterification process performed in the first step. Accordingly, methanol can easily spread in the FAME phase to facilitate the interaction between the methanol and the glycosides remaining in the FAME. These effects are most likely the main cause

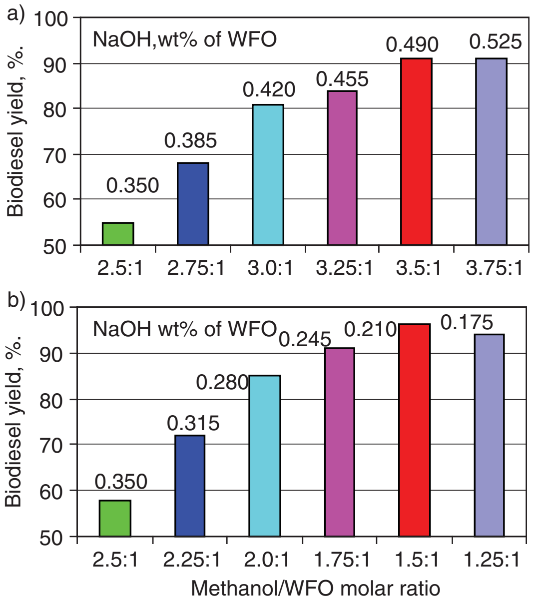

Fig. 3. The effect of using a two-step method on biodiesel yield with different combinations of methanol to WFO molar ratio and NaOH concentration:
a – first step; b – second step

of high biodiesel yields. Therefore, the optimal ratios of MR and NaOH concentration were: 3.5:1 and 0.49 wt% for the first-step and 1.5:1 and 0.21wt% for the second-step, which corresponds to 70% and 30%, respectively. In consequence, the best operating conditions for a two-step transesterification method (the sum of the two steps) were found to be 0.7% of NaOH concentration (7 g/kg or 6.48 g/litre of WFO) and 5:1 methanol to oil molar ratio (213 ml/litre of WFO), with biodiesel yield of 96.4%.

2.3. Fuel properties

2.3.1. Fatty acid composition

The fatty acid composition of the WFO used in this study and its methyl ester are summarized in Table 3. It was found that the fatty acid composition did not change with transesterification. As shown in the table, the total saturated, monounsaturated and polyunsaturated FA contents of WFO were 15.52%, 33.83% and 50.65%, respectively. While the FA contents of biodiesel (waste frying oil methyl ester) were 15.61% saturated, 34.03% monounsaturated and 50.36% polyunsaturated, which were approximately the same as those of WFO, Palmitic (C16:0), Stearic (C18:0), and Palmitoleic (C16:l) and Oleic

Table 3. Fatty acid composition of WFO and its methyl esters

Fatty acid				Molecular weight, kg/kmol		Percent contributions of element, %		
Trivial name	Chemical formula	Symbol	%, by weight	Fatty acid	Contribution	C	H	O
Waste frying oil								
Myristic	$C_{14}H_{28}O_2$	C14:0	0.06	228.38	0.14	73.63	12.36	14.01
Palmitic	$C_{16}H_{32}O_2$	C16:0	11.58	256.43	29.69	74.94	12.58	12.48
Palmitoleic	$C_{16}H_{30}O_2$	C16:1	0.31	254.41	0.79	75.54	11.89	12.58
Margaric	$C_{17}H_{34}O_2$	C17:0	0.09	270.46	0.24	75.50	12.67	11.83
Heptadecenoic	$C_{17}H_{32}O_2$	C17:1	0.06	268.44	0.16	76.06	12.02	11.92
Stearic	$C_{18}H_{36}O_2$	C18:0	3.00	284.48	8.53	76.00	12.76	11.25
Oleic	$C_{18}H_{34}O_2$	C18:1	33.22	282.47	93.84	76.54	12.13	11.33
Linoleic	$C_{18}H_{32}O_2$	C18:2	48.7	280.45	136.58	77.09	11.50	11.41
Linolenic	$C_{18}H_{30}O_2$	C18:3	1.95	278.44	5.43	77.65	10.86	11.49
Arachidic	$C_{20}H_{40}O_2$	C20:0	0.41	312.54	1.28	76.86	12.90	10.24
Gadoleic	$C_{20}H_{38}O_2$	C20:1	0.24	310.52	0.75	77.36	12.34	10.30
Behenic	$C_{22}H_{44}O_2$	C22:0	0.22	340.59	0.75	78.04	12.50	9.45
Lignoceric	$C_{24}H_{48}O_2$	C24:0	0.15	368.65	0.55	78.20	13.12	8.68
saturated (Cn: 0)	–	–	15.52	–	–	–	–	–
monounsaturated (Cn: 1)	–	–	33.83	–	–	–	–	–

Table 3 (*Continued*)

Fatty acid				Molecular weight, kg/kmol		Percent contributions of element, %		
Trivial name	Chemical formula	Symbol	%, by weight	Fatty acid	Contribution	C	H	O
Polyunsaturated (Cn: 2, 3)	–	–	50.65	–	–	–	–	–
Total	–	–	100	–	278.7[a]	76.42[a]	12.28[a]	11.31[a]
Waste frying oil methyl ester								
Methyl myristate	$C_{15}H_{30}O_2$	C14:0	0.06	242.40	0.15	74.32	12.48	13.20
Methyl palmitate	$C_{17}H_{34}O_2$	C16:0	11.64	270.46	31.48	75.50	12.67	11.83
Methyl Palmitoleic	$C_{17}H_{32}O_2$	C16:1	0.31	268.44	0.83	76.06	12.02	11.92
Methyl Margarate	$C_{18}H_{36}O_2$	C17:0	0.08	284.48	0.23	76.00	12.76	11.25
Methyl 10-heptadecenoate	$C_{18}H_{34}O_2$	C17:1	0.04	282.47	0.11	76.54	12.13	11.33
Methyl Stearate	$C_{19}H_{38}O_2$	C18:0	3.03	298.51	9.04	76.45	12.83	10.72
Methyl Oleate	$C_{19}H_{36}O_2$	C18:1	33.44	296.50	99.15	76.97	12.24	10.79
Methyl Linoleate	$C_{19}H_{34}O_2$	C18:2	48.45	294.48	142.68	77.50	11.64	10.87
Methyl Linolenate	$C_{19}H_{32}O_2$	C18:3	1.91	292.46	5.59	78.03	11.03	10.94
Methyl Arachidate	$C_{21}H_{42}O_2$	C20:0	0.41	326.57	1.34	77.24	12.96	9.80
Methyl Gadoleic	$C_{21}H_{40}O_2$	C20:1	0.24	324.55	0.78	77.72	12.42	9.86
Methyl Behenate	$C_{23}H_{46}O_2$	C22:0	0.23	354.62	0.82	77.90	13.08	9.02
Methyl Lignocerate	$C_{25}H_{50}O_2$	C24:0	0.15	382.67	0.15	78.47	13.17	8.36
saturated (Cn: 0)	–	–	15.61	–	–	–	–	–
monounsaturated (Cn: 1)	–	–	34.03	–	–	–	–	–
Polyunsaturated (Cn: 2, 3)	–	–	50.36	–	–	–	–	–
Total	–	–	100	–	292.8[a]	76.82[a]	12.31[a]	10.76[a]

Note: [a] Average value.

(C18:l) acids were the most common saturated and monounsaturated fatty acids, respectively. Similarly, Linoleic (C18:2) and Linolenic (C18:3) were the most common polyunsaturated fatty acids. Van Gerpen (2005), reported that oils containing fatty acids having more than 15 carbon atoms, produced biodiesel of superior quality. Accordingly, from the obtained results in this study, it can be concluded that the WFO is suitable to produce biodiesel.

2.3.2. Chemical and physical properties

The density, viscosity, CN and lower heating value are important properties of biodiesel evaluation for its use as a diesel fuel substitute. The produced biodiesel properties in comparison with WFO, diesel fuel and ASTM D6751-12 and EN 14214:2008 standards are listed in Table 1.

Density is an important parameter for combustion system, because it influences the efficiency of the fuel atomization. The results obtained showed that the density of the biodiesel produced was within the ASTM D6751-12 and EN 14214:2008 standards limits, higher than diesel fuel and lower than WFO. Viscosity is a measure of the internal friction of fuel to flow. One of the main purposes of the transesterification process was to reduce the viscosity of WFO, in order to obtain the properties that are suitable for using it as a fuel. High viscosity of the fuel leads to: poor atomization, large droplet size, and high spray jet penetration. This creates inhomogeneous mixture of the fuel and air in the engine cylinder. As a result, combustion efficiency decreases and the engine performance deteriorate. As shown from Table 1 the kinematics viscosity of biodiesel produced is 4.683 mm^2/s (or cSt), which lies within the ASTM D6751-12 and EN 14214:2008 standards, higher than diesel and less than WFO by about of 7.5 times.

CN is another important property of biodiesel. It is used as diesel fuel ignition quality parameter related to the ignition delay time of a fuel upon injection into the engine cylinder. The higher the CN the shorter the ignition delay time and the better the ignition quality of the fuel and vice versa. CN is measured by comparing the ignition delay of the tested fuel with the reference fuel mixtures, namely n-cetane and hepta methylnonane (15 CN). However, due to the high expense of the CN tests, the CN of the produced biodiesel in this work was calculated according to the FAMEs composition by using equation (9). As shown from Table 1 the CN of the biodiesel is higher than diesel fuel and meets the ASTM D6751-12 standard.

The lower heating value refers to the energy content of the fuel. The calculated LHVs of the tested fuels are listed in Table 1. As the table shows, produced biodiesel contains approximately 12.1% less LHV when compared to diesel fuel. This can be attributed to the presence of oxygen in the biodiesel and to the lower percentage of carbon monoxide $C = 76.82\%$ and hydrogen $H_2 = 12.31\%$ compared to diesel fuel where $C = 87.12\%$, $H_2 = 12.88\%$; because C and H are sources of energy and the oxygen is ballast in fuel.

The IV is a measure of the biodiesel degree of un-saturation. It is well known that, the existence of unsaturated fatty acid element in biodiesel is required as it restricts the biodiesel from solidification. The higher the IV, the more un-saturation is present in the biodiesel. However, the higher degree of un-saturation leads to the formation of deposits or to deterioration of the lubricating in an internal combustion engine due to the polymerization of the glycerides (Mittelbach 1996). Results, obtained from the IV calculations, indicated that the IV of the biodiesel is lower than WFO and meets the ASTM D6751-12 standard (Table 1). Besides, the concentration of linolenic acid in biodiesel does not exceed the EN 14214:2008 standard limit of 12%.

The Acid Value (AV) is a direct measure of FFAs in the biodiesel. The FFAs can lead to corrosion and may be a symptom of water in the fuel. Results obtained from this study indicated that the AV of the biodiesel was found to be within the specifications of ASTM D6751-12 and EN 14214:2008 standards and higher than the AV of diesel fuel (Table 1).

The Carbon Residue (CR) produced after the burning of the fuel and thereafter, deposits on the engine combustion chamber components, which can cause engine knock, blockage in fuel injector nozzles, and corrosion in cylinder-piston assembly. The CR (wt%) of the biodiesel and diesel fuel was measured by a Conradson Carbon Residue (CCR) analyzer, and estimated as the mass ratios of the CR collected after burning and the fuel before burning. The obtained results from this study indicate that, the carbon residue of the biodiesel is higher than that of diesel fuel and slightly higher than ASTM D6751-12 standard. This is because the biodiesel was produced from WFO that contains, probably, impurities, which results in more carbon residue after burning as compared with diesel fuel.

The flash point of the fuel is the temperature at which it will ignite when exposed to a flame or spark. In the present study, the flash point of the biodiesel is higher than diesel fuel, ASTM D6751-12 and EN 14214:2008 standards limits, as shown in Table 1. Therefore, using biodiesel as a fuel is much safer than diesel, from the point of view of self-ignition and fire hazards at high temperatures during transportation and storage.

3. Engine tests

With the increase of the use of biodiesel around the world; numerous studies have been conducted in order to investigate the performance of diesel engines using biodiesel, in pure form or blended with diesel fuel. Most of these studies reported that engine brake power and brake thermal efficiency are lower and brake specific fuel consumption is higher when using cooking oil methyl ester and its blends than diesel fuel, especially with increase of biodiesel in the blends (Canakci *et al.* 2009; Rao *et al.* 2008; Utlu, Koçak 2008; Murillo *et al.* 2007; Sudhir *et al.* 2007; Dorado *et al.* 2003; Canakci, Van Gerpen 2003; Guo *et al.* 2002). However, some studies reported that biodiesel can cause a slightly higher engine power than diesel fuel (Gonzalez Gomez *et al.* 2000; Usta *et al.* 2005; Agarwal, Das 2000). These discrepancies can be related to the fact that, the biodiesel has different physical and chemical properties, which depends on the feedstock used to produce it, from those of diesel fuel, which cause changes in engine performance. Therefore, to investigate the behaviour of the produced biodiesel as an alternative diesel fuel, the pure biodiesel and its blends with diesel fuel, as well as the diesel fuel, as a base fuel for comparison, were tested on a diesel engine to estimate the engine performance parameters.

3.1. Experimental apparatus and procedures

Experiments were conducted on a single cylinder four-stroke water-cooled diesel engine developing 6 kW at 1500 rpm. The schematic of experimental set-up is shown in Fig. 4. The fuels used were: pure diesel fuel (B0), pure biodiesel (B100) and biodiesel blends with diesel, which are: 95% B0 and 5% WFO (B5), 90% B0 and 10% WFO (B10), 80% B0 and 20% WFO (B20), in the volume basis. Time taken for fuel consumption was measured with the help of a digital stop watch. An orifice meter was used to measure air consumption of the engine with the help of inclined U-tube manometer. The air tank fixed on the inlet side of an engine maintains a constant airflow through the orifice meter. The engine was coupled by a flat belt to an electric dynamometer for load

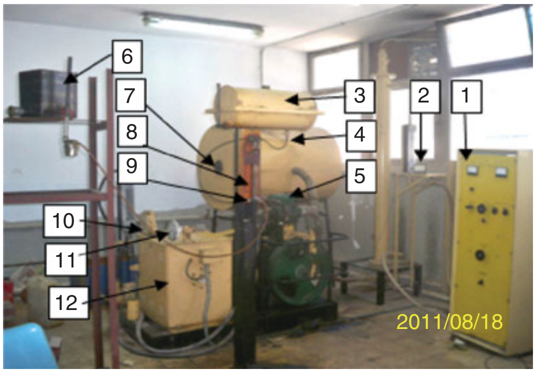

Fig. 4. The schematic diagram of the engine test bed: 1 – control panel; 2 – temperature indicator 3 – base fuel tank; 4 – air tank; 5 – diesel engine; 6 – fuel blends tank; 7 – air orifice; 8 – burette fuel measurement; 9 – three way valve; 10 – load indicator; 11 – engine rotation speed indicator; 12 – electrical dynamometer

measurement. Engine was run at several speeds from 800 to 1400 rpm at 50% of full load. The engine brake power, brake specific fuel consumption, brake thermal efficiency and air to fuel ratio were calculated. Tests were executed without carrying out any modification on the engine or its fuel injection system. To obtain a base line test, the engine was run first on diesel fuel and then on B100 and on fuel blends. After each fuel was tested, fuel system parts were drained prior to filling them with the next one. Then the engine was operated at least 15 minutes on the new fuel to remove any of the remaining fuel in the engine fuel system from the previous test. Each test was repeated three times and the average value was recorded.

3.2. Engine test results

The engine tests are very important to investigate the effects of the tested fuels on the engine performance. Because, the results of these tests indicate, whether or not, the engine operates efficiently without any problems when using the tested fuel. Therefore, the following engine performance parameters were determined: equivalence air to fuel ratio, brake power, brake specific fuel consumption and brake thermal efficiency.

3.2.1. Equivalence air fuel ratio

The equivalence AFR (φ) defines the mixture composition that is, fuel-rich or lean mixture and defined as the ratio of the actual AFR to the stoichiometric AFR:

$$\varphi = \frac{(AFR)_{act}}{(AFR)_{st.b}}; \tag{10}$$

$$(AFR)_{st.b} = \frac{\sum(\chi_i \cdot \rho_i \cdot AFR_i)}{\sum(\chi_i \cdot \rho_i)}. \tag{11}$$

The equivalence AFR as a function of the engine speed for different tested fuels is shown in Fig. 5. From the figure, it can be observed that the AFR decreases as the engine speed increases for all fuels. This decrease can be related to the decrease of the actual AFR, because the fuel mass flow rate increases with the increase of the engine speed, while the mass flow rate of air and the stoichiometric AFR remain constant for each engine speed and for each fuel respectively, and as a result the equivalence AFR decreases. On the other hand, when the engine operates on pure biodiesel the equivalence AFR is close to that of diesel fuel, whereas, when the engine operates on the fuel blends the equivalence AFR is lower than that of diesel fuel. The amount of decrease is directly proportional to the increase of the biodiesel in the fuel blends. This can be attributed to the following factors: the stoichiometric AFR and the LHV of the B100, B5, B10 and B20 are less than diesel fuel by about of 12.12, 0.63, 1.26 and 2.52% for AFRst and 12.1, 0.6, 1.21 and 2.42% for LHV, respectively. Therefore, when using pure biodiesel, the increase of the fuel consumption due to the decrease of the LHV, compensates the decrease of the stoichiometric AFR, and hence, the equivalence AFR is similar to that of diesel fuel. On the other hand, when using fuel blends, the effect of the fuel consumption increase, which leads to decrease of the actual AFR, or the equivalence AFR is more than the decrease of the stoichiometric AFR and therefore, the equivalence AFR decreases as compared with diesel fuel.

3.2.2. Brake power

Brake power produced by the engine and absorbed by the dynamometer is directly proportional to the brake torque and engine rotation speed, which was calculated by the following equation:

$$P_b = \frac{T \cdot n}{9549.29}; \tag{12}$$

$$T = F \cdot L, \tag{13}$$

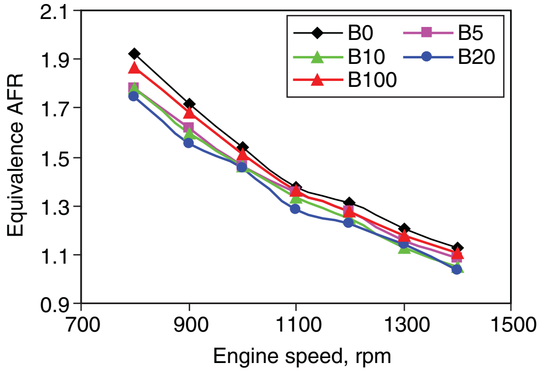

Fig. 5. The effect of tested fuels on equivalence air fuel ratio at different engine speed

where: P_b is the brake power (kW); n is the engine rotation speed (rpm); T is the brake torque (N m); F is the applied load (N); L is the load lever connected to the balance weights (m).

The effect of the tested fuels on brake power at different engine speeds is presented in Fig. 6. The Fig. 6 indicates that, the brake power increases with the increase of engine speed for all tested fuels, due to the increase of engine applied load. Also, from the figure it can be observed that the brake power of B100 is close to that of diesel fuel and slightly higher than diesel when the engine operates on a fuel blends. This might be explained as follows: the variations of the brake power reflected the variations in the lower heating values and densities of the tested fuels. The densities of the biodiesel and its blends with diesel fuel are higher, and the lower heating values are lower than that of diesel fuel. Therefore, the higher density of the biodiesel, which leads to a higher mass flow rate of biodiesel than diesel fuel, compensates the lower energy content in the biodiesel and accordingly a small difference in brake power occur when using B100 and diesel fuel. Whereas, the increase of the brake power, when using fuel blends, may be related to presence of oxygen in the biodiesel, which enhance the fuel combustion process, accordingly the brake power increased.

3.2.3. Brake specific fuel consumption

The Brake Specific Fuel Consumption (BSFC) depends on the fuel mass flow rate and on the brake power as presented by the following equation:

$$BSFC = \frac{m_f}{P_b} \cdot 1000, \tag{14}$$

where: $BSFC$ is the brake specific fuel consumption (g/kWh); and m_f is fuel mass flow rate (kg/h).

The variation of BSFC for different fuels under various engine speeds is shown in Fig. 7. As the figure shows, the BSFC decreases as the engine speed increased up to 1300 rpm and then increases. This might be due the decrease of both: heat losses from the air-fuel mixture to the combustion chamber walls and hydraulic losses in the intake system, resulting in a higher increase of the brake power than the increase of the fuel mass flow rate due to increase of the engine speed. Further increase of the engine speed leads to increase of the friction losses in the piston-cylinder assembly and the hydraulic losses, resulting in a slower increase of the brake power than of the fuel mass flow rate, accordingly increase in BSFC. Moreover, from the figure, it can be observed that, the BSFC increases with the increase of biodiesel percentage in the fuel blends for all engine speeds. As shown from Fig. 6, the differences between the brake power of the diesel fuel, B100, B5, B10 and B20 are very small, accordingly the effect of the brake power on the BSFC can be considered as constant. Therefore, the increase of the BSFC when the engine operates on biodiesel or on its blends can be attributed to the increase of the fuel mass flow rate due to its higher density and viscosity as compared with diesel fuel (Table 1).

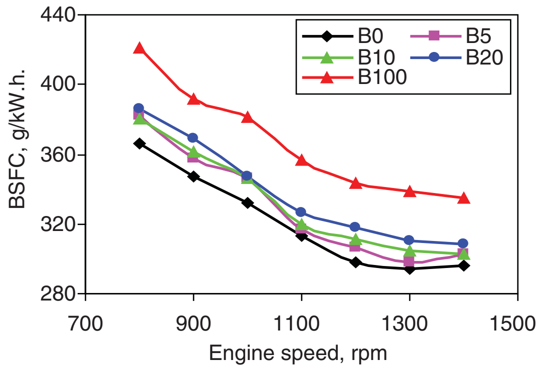

Fig. 7. The effect of the tested fuels on the brake specific fuel consumption with different engine speed

3.2.4. Brake thermal efficiency

The Brake Thermal Efficiency (BTE) is inversely proportional to the brake specific fuel consumption,

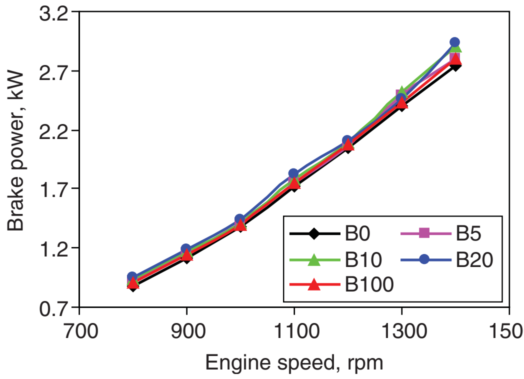

Fig. 6. The effect of the tested fuels on brake power as a function of the engine speed

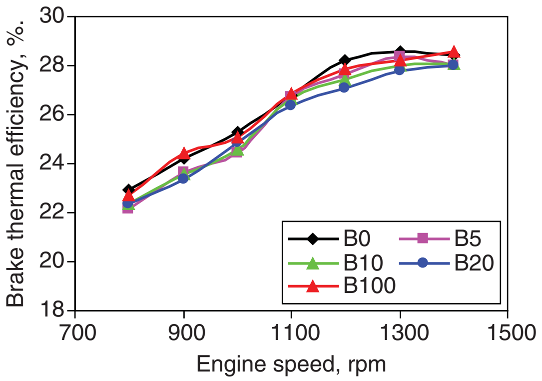

Fig. 8. The effect of tested fuels on the brake thermal efficiency as a function of the engine

Table 4. The deviations of the biodiesel and fuel blends as compared with diesel fuel based on an average values

Tested fuels	AFRst	LHV, MJ/kg	Density, kg/m^3	Equivalence AFR	Power, kW	BSFC, g/kWh	BTE, %
B0	14.44	42.820	846.6	1.46	1.756	321	26.37
B5	14.35	42.549	848.61	1.39	1.798	330	25.85
D, %	−0.63	−0.63	0.24	−4.63	2.54	2.7	−2.06
B10	14.26	42.280	850.62	1.37	1.828	332	25.80
D, %	−1.26	−1.26	0.47	−6.28	4.03	3.5	−2.22
B20	14.08	41.745	854.64	1.35	1.843	338	25.59
D, %	−2.52	−2.51	0.95	−7.86	5.15	5.2	−2.68
B100	12.69	37.64	886.80	1.43	1.786	367	26.23
D, %	−12.12	−12.10	4.75	−2.08	1.73	14.3	−0.47
Average value	–	–	–	−5.21	3.36	6.4	−1.76

Note: D – deviation.

and to the lower heating value of the fuel, as defined by the following equation:

$$\eta_b = \frac{3600}{BSFC} \cdot LHV, \tag{15}$$

where: LHV is the lower heating value of fuel (MJ/kg); $BSFC$ is brake specific fuel consumption (g/kWh).

The effect of the tested fuels on BTE with different engine speeds is shown in Fig. 8. It can be seen from the figure that, the BTE increases with the increase of the engine speed for all tested fuels. This increase can be attributed to the same reasons that affect the increases of the brake power. Additionally, as the figure shows, the BTE of B100 looks like diesel fuel, while it decreases with the increase of the biodiesel percentage in the fuel blends for all engine speeds. This can be attributed to the following factors: the LHVs of the biodiesel and a fuel blends are lower than that of diesel fuel, while the BSFC is higher (Fig. 7). Therefore, the BTE decreases with the increase of BSFC and increases with the decrease of the LHV. The combined effect of the two opposite factors on the BTE, when the engine operates on pure biodiesel, maintains the BTE of the biodiesel close to that of diesel fuel. On the other hand, for the fuel blends, the effect of BSFC increase is more pronounced than the LHV decrease, consequently the BTE decreases.

The higher decrease of 8% occurs when the engine operates on B20. The behaviour of the brake thermal efficiency is inverse to the behaviour of the BSFC for each fuel.

Conclusions

In this experimental study the waste frying oil was converted into biodiesel by one-step and two-step base-catalyzed transesterification methods, with different NaOH concentrations and methanol to oil molar ratios. In the first method the reaction conditions were optimized and adapted, as reference conditions, to conduct the second method. In addition, an experimental study was performed on engine performance to evaluate the produced biodiesel as a fuel for a diesel engine in comparison with diesel fuel. Based on the experimental results of this study, the following conclusions can be drawn:

1) The optimum conditions for methanol to oil molar ratio and NaOH concentration were 5:1 and 0.70 wt% of WFO for one-step method and 3.5:1 and 0.49 wt% for the first step and 1.5:1 and 0.21 wt% for the second step, of a two-step method, respectively.
2) These conditions provided biodiesel yield of 95% and 96.4% for one-step and two-step transesterification methods, respectively. The two-step transesterification method enhances the yields of biodiesel by about of 2% as compared with the one-step transesterification method.
3) The fatty acid compositions of the WFO and the produced biodiesel were found to be the same. The major FA components observed by GC were Palmitic acid (C16:0), Oleic acid (C18:l) and Linoleic acid (C18:2).
4) The density, viscosity and acid value of the produced biodiesel are lower than that of WFO and higher than that of diesel fuel. Also, the molecular weight, the cetane number and the flash point of the biodiesel are higher than diesel fuel, while the lower LHV and air to fuel ratio are lower. On the other hand, the fuel properties, of the biodiesel, such as: cetane number, viscosity, flash point, carbon residue, acid value and Lino-

lenic FAME were comparable to those of recommended properties by ASTM D6751-12 and EN 14214:2008 standards.

5) The experiments on engine performance indicated that the engine brake power and the BSFC for biodiesel and its blends were higher than that of diesel fuel by about of (average values) 3.4% and 6.4%, respectively. While the equivalence air to fuel ratio and the brake thermal efficiency are lower by about of 5.2% and 1.8%, respectively (Table 4).

Generally, the biodiesel from WFO could be a competitive alternative to diesel fuel from the point of view of: the fuel properties and its successful application on a diesel engine without any problems or any modification.

Acknowledgements

Financial support provided by the Al Balqa Applied University for this research is gratefully acknowledged. Also, the author is grateful to Eng. Hamdy Al-Zoby from the faculty of engineering technology for technical assistance.

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