Biodiesel from Waste Olive Oil: Transesterification Kinetics, Exhaust Emissions and Fuel Consumption

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Introduction

Biodiesel is defined as "a fuel comprised of mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats" [1]. Transesterification (also called alcoholysis) of triglycerides [2] and jojoba oilwax [3] for biodiesel manufacture has been studied in our research group in the past few years. The European Union has issued Directive 2003/30/EC, which mandates the use of biofuels in a percentage ranging from 2% in 2005 to 5.75% in 2010 (calculated on the basis of energy content), for all transportation fuels marketed within the member states. It is expected that a significant portion of this amount will be biodiesel. However, although the literature concerning the production of biodiesel has increased dramatically in the last 5 years [4, 5], data related to the kinetics of transesterification are rather scarce: [6] presented the kinetics and final state of methano-, ethano- and butanolysis of cottonseed, peanut, soybean and sunflower oils catalyzed by sodium hydroxide and methoxide or sulphuric acid, and [7] studied the kinetics of methanolysis of sunflower oil catalyzed with KOH. The effect of water on the kinetics of cotton oil ethanolysis catalyzed by KOH [8], and the kinetics of the non-catalytic transesterification of soybean oil at 220°C and 230°C [9], was described. The kinetics of transesterification of rapeseed oil to biodiesel fuel in supercritical methanol without any catalyst was described [10], and [11] described the kinetics and mechanism of the KOH catalyzed methanolysis of rapeseed oil for biodiesel production. Moreover, the kinetics of methoxide base-catalyzed methanolysis of

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soybean oil at 40°C was studied [12]. To the best of our understanding, any data have been published to date on the kinetics of the transesterification of used olive frying oil catalyzed by sodium methoxide at 60°C to produce biodiesel, which is the first aim of this paper.

In Spain, edible vegetable oil consumption is approximately 600 ML/year. Most of this oil (70%) is olive oil that is mainly used for deep-frying processes. According to the Spanish National Institute of Statistics, about 74 ML of waste olive oil are collected per year, which is an approximate value since most of the household waste frying oil is thrown through the drainage. Transesterification of waste olive oil to produce biodiesel could decrease the waste disposal problem. Studies concerning the exhaust emissions produced by the combustion of pure waste olive oil biodiesel have been published recently [13], but no data exist to date on the emissions produced by the combustion of blends of waste olive frying oil biodiesel in 5% vol and fossil diesel fuel. The Spanish Government allows petroleum product operators to blend biodiesel up to 5% vol with conventional diesel fuel without the need to legally declare this blending.

Nitric oxide (NO) and nitrogen dioxide (NO_2) are very important in polluted air. Collectively designated NO_x, high NO_x concentrations can cause severe air quality impoverishment. NO_x enters the atmosphere as a result of the combustion of fossil fuels in internal combustion engines. Like carbon monoxide, NO attach to haemoglobin and reduces oxygen transport efficiency. Particulate matter (PM) exhaust emissions are also of great concern, since they are involved in acid rain processes and respiratory diseases. Substantial reduction in PM emissions can be obtained by addition of biodiesel to diesel fuel. The PM reduction appears to be related to the amount of oxygen content in the fuel blend [14]. This paper also reported the exhaust emissions from ternary blends of waste olive oil biodiesel (5% vol), ethanol (5% vol) and fossil diesel fuel, the so called BE-diesel.

Although some studies have been published recently on exhaust emissions of BE-diesel [15], no data exits on the use of the blends described in our paper, especially with the use of waste olive oil biodiesel. Ethanol is a low cost oxygenate of vegetal origin with high oxygen content. However, there are many technical barriers to the direct use of ethanol in diesel fuel due to the low cetane number of ethanol, and the poor solubility in cold climates. In fact, diesel engines cannot operate normally on ethanol-diesel blends without special additives [16]. Biodiesel is known to act as an emulsifier for ethanol, and blending biodiesel and ethanol into a conventional diesel fuel greatly improved the solubility of ethanol in diesel fuel over a wide range of temperatures [17].

Experimental

Methanol, tetrahydrofuran (THF), sodium, hydrochloric acid and anhydrous sodium sulphate were all commercial grade and used without further purification. The oil transesterified in all the experiments was waste olive frying oil of domestic origin.

For the production of biodiesel from waste olive oil, the method of transesterification with methanol and basic catalyst (sodium methoxide) was used in the following conditions: molar ratio methanol/oil: 7.85/1; 60°C; 600 rpm, amount of catalyst from 1.4 to 2.8% wt of the oil. The total quantity of the oil 760 mL (700 g) was placed in the reactor with part of the methanol, 155 mL (120.9 g, 3.78 mol). The stirring and the heating were switched on. The rest of the methanol, 100 mL (78 g, 2.44 mol) was used for the preparation of the catalyst by reaction with 4.35 g (0.189 mol) of metallic sodium. After total dissolution of the sodium, the catalyst was added to the reactor were the desired temperature was already achieved. A slight increase of temperature to 64°C was observed after the addition of the catalyst which was soon controlled to 60°C. The reactor was left for the time specified for the reaction, and then the heating and the stirring were switched off. One hour after the refrigerating water was also switched off, and the two phases were decanted overnight. After the distillation of the methanol in both phases, the glycerine phase was neutralized with 14.5 mL of concentrated (37% wt) hydrochloric acid. The biodiesel phase was neutralized in a decanting funnel with two washings with diluted aqueous solution of hydrochloric acid, and afterwards it was washed with diluted aqueous solution of sodium chloride and three times with water. The biodiesel was then dried with anhydrous sodium sulphate and filtered. For the analysis of the content in glycerol and mono-, di- and triglycerides according to the European standard EN 14105 [18], a gas chromatograph Hewlett Packard HP 6890 series GC system was used, in connection with a mass spectrometer Hewlett Packard 5973 Mass Selective Detector, including an automated system of sample injection. The results of these analyses are summarized in Table 1.

The kinetics experiments have been carried out with the same amounts of reagents, using the same procedure. 10 mL samples, taken at 2, 5, 10, 15, 25, 40 and 60 min

Table 1 Properties of the biodiesel of waste olive oil

Analysis	Biodiesel	Max	Min	Units	Standard
Free glycerol	0.03	0.02		% Mass	EN 14105
Monoglycerides	1.29	0.80		% Mass	EN 14105
Diglycerides	0.17	0.20		% Mass	EN 14105
Triglycerides	<0.05	0.20		% Mass	EN 14105
Total glycerol	0.36	0.25		% Mass	EN 14105
Water and sediments	<0.05	0.05	–	% Vol	ASTM D 1796
Density at 15°C	880	900	860	kg/m^3	ASTM D 4052
Sulfated ash content	<0.005	0.02		% Mass	ASTM D 482
Copper strip corrosion	1a	Class 1	Class	ASTM D130	
Total contamination	24.0	24.0		mg/kg	EN 12662
Flash point	141.9	–	120	°C	ASTM D 92
Cloud point	5			°C	ASTM D 2500
Cold filter plugging point	−5.0			°C	EN 116
Kinematic viscosity at 40°C	5.44	5.00	3.50	mm^2/s	ASTM D 445
Higher calorific value	9748.6			cal/g	ASTM D240
Cetane number	57.9		51		ASTM D 613

were immediately neutralized with 1:1 hydrochloric acid (2 mL). Methanol was evaporated from the sample using a rotary evaporator. 10 mL of THF were added, and this solution was dried with anhydrous sodium sulphate. 200 mg (exactly weighed) were used for the analysis of free glycerol, and mono-, di- and triglycerides according to the standard EN 14105 [18] (instead of the 100 mg to balance for the addition of the THF). The Fatty Acids Methyl Esters (FAME) content was calculated from the analyses and the mass balance in each kinetic sample.

Some physicochemical properties of the biodiesel prepared according to this recipe were determined in a preliminary study of the feasibility of use this biodiesel as a fuel in diesel engines. The higher calorific value was measured after the ASTM standard D 240.

The cetane number was calculated from the time needed for the rise of the pressure by 2 mbar in the fuel ignition chamber, (ASTM D 613). The equipment was from Fuel Tech. Co. and the cooling water circulation (Circulating System 253) from the Precision Co.

The fossil diesel was mixed with the waste olive oil biodiesel. Blends containing 5% vol biodiesel, were chosen in order to prepare samples to fulfill the requirements of EN 590 specification (max. biodiesel content 5% vol) and because it was a reasonable percentage within the requirements of Directive 2003/30/EC (maximum 5.75% based on lower heating value). The engine tests were made in a single cylinder diesel Petter AVL-LAB engine; operating characteristics are given in Fig. 1. Apart from the engine, the system consists of an electric dynamometer, some heat exchangers for the lubricants and a control panel. The dynamometer was connected with the rotor and was originally moving the same way in order to help the engine to start, but later the dynamometer was used as a power generator transforming the mechanical power of the engine to electrical power. In this way we were able to adjust the charge of the engine by changing the potential in the dynamometer. The parameters controlled

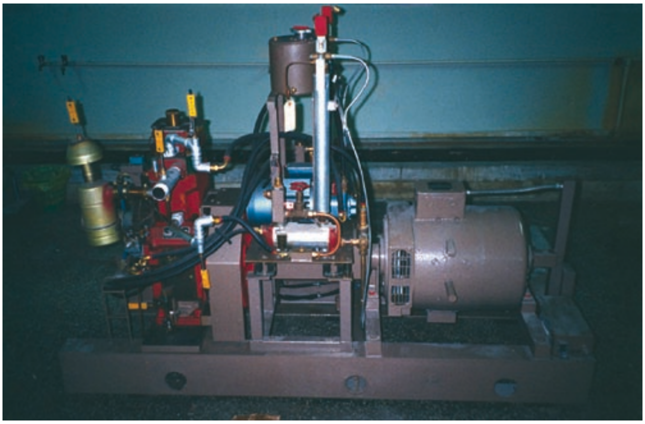

Fig. 1 Test AVL-LAB engine used in the emissions and fuel consumption experiments. Type: single cylinder direct injection, speed: 1,500 rpm, compression: 19:1, volume: 533 cm^3, maximum power: 5 hp (3.8 kW)

from the control panel are the charge (resistance) of the dynamometer, the temperature of the air at the inlet and the outlet, and the temperature of the inlet and outlet of the lubricant and the cooling water. The experiment consisted of measurement of NO_x and PM emissions and fuel consumption for different charges of the engine from 0% to 100% (3.8 kW).

The analyzer (MEXA-754 GE, Horiba) was used to calculate the amounts of NO_x in the exhaust gases. The most important aspects of this analyzer were: exhaust gases measured, NO, NO_2; units, ppm; range, (0–5,000) ppm; accuracy, ±1%. The analyzer was connected to the engine through heated lines of exhaust transport from Signal Instruments Co (type 530/540) and a pre-filter unit (Signal Instruments Co, Pre-filter Unit 333).

For the analysis of particles in the exhaust gases, the equipment of Joy Manufacturing Co.; recommended by the Western Precipitation Division was used. The filters where of Whatman type 934-AH.

Results and Discussion

Biodiesel Quality

The composition of biodiesel after the EN 14214 [1] specification is summarized in Table 1. The transesterification reaction rate is much higher than it was originally estimated. After the first 10 min of the addition of the catalyst to the reactor, an almost quantitative conversion of TG to FAME and glycerol takes place. All the time that the reactor is left running after this initial time, the reactions are reversible reactions, and the reaction mixture is slowly moving towards equilibrium. The chromatograms of the kinetic samples show an initial quantitative conversion of TG to FAME but after the first minutes the monoglycerides MG (1.29% wt) and diglycerides DG (0.17% wt) reappear. However, only MG are out of the specification (1.29% wt, max. 0.80% wt), and consequently also the total glycerol G (0.03% wt, max. 0.02% wt). The biodiesel produced meets most of the specifications required by the Technical Regulation EN 14214.

Kinetic Experiment

The % wt of TG, DG, MG, G and FAME are plotted against time in Fig. 2. The transesterification reaction is very quick at 60°C and almost all TG were converted after the first 5 min; MG and DG were transient intermediate species, always at very low concentrations.

The transesterification reaction could be considered as an irreversible second order reaction (first order in TG and first order in methanol) which had been solved as follows. The transesterification reaction had the general form:

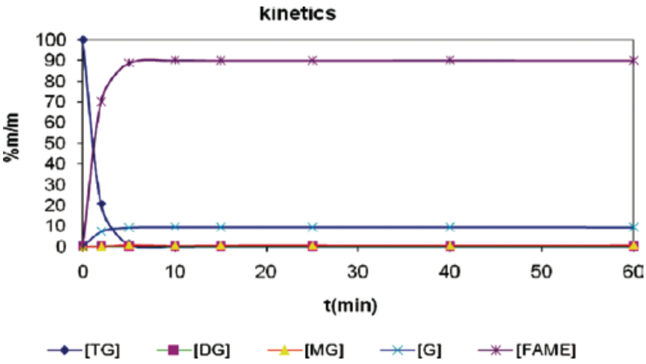

Fig. 2 Concentrations of mono-, di-, triglycerides, FAME and glycerol vs. time in the kinetic experiments

$$A + bB \xrightarrow{k} \text{products}$$

Here the function that expresses the rate of reaction vs. time was [19]:

$$k \cdot t \cdot b \cdot C_{A_0}\left(M-1\right) = \ln\frac{C_B}{b \cdot M \cdot C_A}, \text{where M} = \frac{C_{B0}}{bC_{A0}}.$$

The simplified reaction was:

$$TG + 3CH_3OH \xrightarrow{k} G + 3FAME$$

Here C_A was the concentration of TG, C_B the concentration of methanol, b = 3. 760 mL (699.2 g) of waste olive oil (mean mw 885.43 g/mol), and 255 mL (201.45 g) of methanol (a total of 1015 mL) was introduced to the reactor. Thus, the mol number *n* and the initial concentrations C_{I0} are: n_{A0} = 0.79 mol; C_{A0} = 0.78 mol/L; n_{B0} = 6.3 mol; C_{B0} = 6.20 mol/L. M = 2.65.

Consequently, the second order reaction equation remains as follows:

$$\mathrm{k} \cdot \mathrm{t} \cdot 3 \cdot 0.78 \cdot \left(2.65 - 1\right) = \ln\frac{C_B}{3 \cdot 2.65 \cdot C_A}$$

This second order kinetic equation was solved using the mass fractions of TG and methanol. The mass fraction of methanol was calculated in every point from the difference of the measured mass fractions of G, MG, DG, TG and FAME. The kinetic plot of $\ln(C_{MeOH}/aC_{TG})$ vs. time gave a straight line (Fig. 3). The 95% confidence limits for the intercept and slope of the straight line are:

Slope: 0.2245 ± 0.0521

Intercept: –0.8571 ± 0.1621

The resulting rate constant *k* is 0.2245 $L \cdot mol^{-1} \cdot min^{-1}$. The transesterification reaction of used olive frying oil with methanol catalyzed with sodium methoxide, follows the equation:

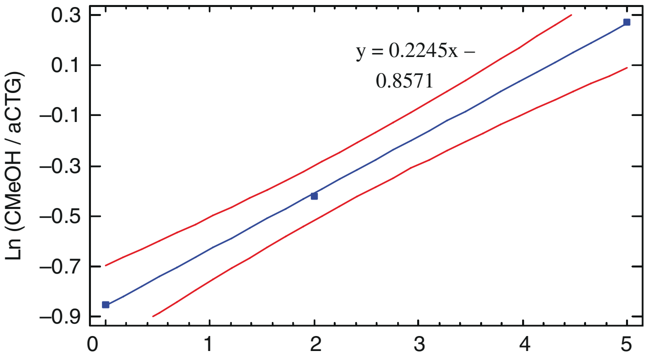

Fig. 3 Kinetic plot of Ln ($C_{MeOH/}$a C_{TG}) vs. time for the second order kinetics transesterification reaction

$$-r_{TG} = 0.2245[TG][MeOH](\mathrm{mol{\cdot}L^{-1}{\cdot}min^{-1}})$$

Exhaust Emissions and Fuel Consumption

The fossil diesel was mixed with the waste olive oil biodiesel, and blends containing 5% vol biodiesel were prepared. Also, samples were prepared that contained 5% vol of ethanol to compare the performance of BE-diesel fuel with fossil diesel and biodiesel-fossil diesel blends. The results of these tests are summarized in Tables 2 through 4.

The effect of oxygenated fuels blends on NO_x emissions is complex and not conclusive. Cetane number, fuel density and aromatic fuel composition can influence NO_x emissions. Many studies indicate that oxygenated fuel blends could cause slight increases in NO_x emissions [17]. However, in our work the reduction of NO_x exhaust emissions was significant when using blends of fossil diesel and waste olive oil biodiesel (–11.7%), and in good agreement with previous results [13]. It was very interesting with ternary blends of BE-diesel (–32.7%) although previous

Table 2 NO_x Exhaust emissions reduction (%)

Sample	Base fuel	Base fuel + 5% waste olive oil biodiesel
Diesel	0	–11.7
Diesel + 5% vol ethanol	–15.3	–32.7

Table 3 Particulate matter (PM) exhaust emissions reduction (%)

Sample	Base fuel	Base fuel + 5% waste olive oil biodiesel
Diesel	0	–6.1
Diesel + 5% vol ethanol	–13.1	+2.0

Table 4 Mass consumption (g/h) and energy consumption (MJ/h) vs. engine charge (kW) of blends of diesel and diesel + 5% vol ethanol with waste olive oil biodiesel

Sample		0 kW	0.08 kW	0.95 kW	1.90 kW	2.85 kW	3.80 kW
Diesel	g/h	485.9	472.4	556.1	638.4	710.1	783.4
	MJ/h	21.7	21.1	24.9	28.5	31.8	35.0
Diesel + 5% vol waste olive oil biodiesel	g/h	405.2	408.1	512.8	571.0	617.4	713.1
	MJ/h	18.1	18.2	22.9	25.4	27.6	31.8
	%	−16.6	−13.7	−8.0	−10.9	−13.2	−9.1
Diesel + 5% vol ethanol	g/h	482.6	473.9	558.0	663.8	704.3	826.1
	MJ/h	21.7	21.4	25.2	29.9	31.8	37.3
	%	0	+1.4	+1.2	+4.9	0	+6.6
Diesel + 5% vol ethanol + 5% vol waste olive oil biodiesel	g/h	426.1	418.8	504.3	588.4	624.6	688.4
	MJ/h	19.1	18.8	22.7	26.4	28.0	31.0
	%	−12.0	−10.9	−8.8	−7.4	−11.9	−11.4

results with BE-diesel fuel showed an increase in NO_x emissions, albeit for a different ethanol-biodiesel-diesel fuel ratio [15]. Oxygenate diesel fuel blends are known to reduce total PM emissions, although the mechanisms are not clear. Soot formation mainly takes place in the fuel-rich zone at high temperatures and pressures, specifically within the core region of the fuel spray.

It is commonly assumed that oxygenates blended with diesel fuel effectively deliver oxygen to the pyrolysis zone of the burning diesel spray, resulting in reduced PM generation. The blends of fossil diesel + biodiesel and fossil diesel + ethanol shows good results in the reduction of PM (−6.1% and −13.1%, respectively), but the ternary blends of BE-diesel shows an increase of PM (+2.0%), in contrast to previous reported results [15]. This difference could be explained by the lower amount of biodiesel used in our experiments that described in the literature [15]. From a practical point of view, the advantage of reducing NO_x emissions by one third should be balanced against a slight increase in the PM emission when using this ternary BE-diesel fuel blend.

The binary blends of fossil diesel and biodiesel show a decrease in the consumption from −16.6% at the lowest engine power to −9.1% at the highest power. On the contrary, the binary blends of fossil diesel and ethanol always show an increase in fuel consumption. However, the ternary blends of BE-diesel fuel show a reduction in the fuel consumption at all engine powers tested. This, coupled with the reduction in the NO_x emissions, makes this fuel a good promise for diesel cars in a near future.

Conclusions

The transesterification reaction of waste olive oil with methanol, catalysed with sodium methoxide, to produce biodiesel follows a first order kinetics in methanol and in triglycerides, with a rate constant of $k = 0.2245\ \text{L mol}^{-1}\ \text{min}^{-1}$. The reaction time should be optimized to avoid the reversible reactions that increase the amount of monoglycerides in the final products.

When added in a 5% vol to conventional fossil diesel, biodiesel fuel reduces NO_x and PM emissions, especially when using ternary blends of fossil diesel, biodiesel (5% vol) and ethanol (5% vol), BE-diesel fuel. It also significantly reduces the fuel consumption of the engine.

References

1. European Committee for Standardization (DIN) (2003) Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods. European Standard EN 14214
2. Alcantara R, Amores J, Canoira L, Fidalgo E, Franco MJ, Navarro A (2000) Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow. Biomass and Bioenergy 18:515–527
3. Alcantara R, Canoira L, Garcia-Martinez MJ Carrasco J (2006) Biodiesel from jojoba oil-wax: transesterification with methanol and properties as a fuel. Biomass and Bioenergy 30:76–81
4. Fangrui Ma, Hanna MA (1999) Biodiesel production: a review. Bioresource Technology 70:1–15
5. Meher LC, Vidya Sagar D, Naik SN (2006) Technical aspects of biodiesel production by transesterification: a review. Renewable and Sustainable Energy Reviews 10:248–268
6. Freedman B, Butterfield RO, Pryde EH (1986) Transesterification kinetics of soybean oil. Journal of the American Oil Chemist Society 63:1375–1380
7. Mittelbach M, Trathnigg B (1990) Kinetics of alkaline catalyzed methanolysis of sunflower oil. Fat Science Technology 92:145–148
8. Bikou E, Louloudi A, Papayannakos N (1999) The effect of water on the transesterification kinetics of cotton oil. Chemical Engineering and Technology 22:70–75
9. Diasakou M, Louloudi A, Papayannakos N (1998) Kinetics of the non catalytic transesterification of soybean oil. Fuel 77:1297–1302
10. Kusdiana D, Saka S (2001) Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel 80:693–698
11. Komers K, Skopal F, Stloukal R, Machek J (2002) Kinetics and mechanism of the KOH-catalyzed methanolysis of rapeseed oil for biodiesel production. European Journal of Lipid Science and Technology 104:728–737
12. Boocock DGB, Konar SK, Mao V, Sidi H (1996) Biomass and Bioenergy 11:43–50
13. Dorado MP, Ballesteros E, Arnal JM, Gomez J, Lopez FJ (2003) Exhaust emissions from a diesel engine fueled with transesterified waste olive oil. Fuel 82:1311–1315
14. Shi X, Yu Y, He H, Shuai S, Wang J, Li R (2005) Emission characteristics using methyl soyate-ethanol-diesel fuel blends on a diesel engine. Fuel 84:1543–1549
15. Shi X, Pang X, Mu Y, He H, Shuai S, Wang J, Chen H, Li R (2006) Emission reduction potential of using ethanol-biodiesel-diesel fuel blend on a heavy-duty diesel engine. Atmospheric Environment 40:2567–2574
16. McCormick RL, Parish R (2001) Technical barriers to the use of ethanol in diesel fuel. Milestone report to NREL MP-540–32674
17. McCormick RL, Michael S, Graboski TL, Alleman A, Herring M (2001) Impact of biodiesel source material and chemical structure on emissions of criteria pollutants from a heavy-duty engine. Environmental Science and Technology 35:1742–1747
18. Fat and oil derivatives. Fatty Acid Methyl Esters (FAME) (2003) Determination of free and total glycerol and mon-, di-, triglyceride content. Reference method EN 14105
19. Levenspiel O (1999) Chemical Reaction Engineering. 3rd ed. Wiley, New York