



Study of esterification and transesterification in biodiesel production from used frying oils in a closed system

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ARTICLE INFO

Article history:

Received 19 October 2009

Received in revised form 18 March 2010

Accepted 19 March 2010

Keywords:

Used frying oils

Esterification

Transesterification

Closed system

Kinetics

Polar FAME

ABSTRACT

Used frying oils are a good alternative for biodiesel production but their treatment is more complex than fresh vegetable oils. Used frying oils contain a large amount of free fatty acids, so an esterification step is necessary before transesterification. This reaction is usually carried out in batch reactors with pressure and temperature conditions (ambient pressure and 60 °C) where the esterification reaction acts as the limiting step of the production. The aim of this work was to investigate the acidity removal and the subsequent transesterification at different temperatures and mole ratios in a batch reactor in order to improve the biodiesel production from used frying oils.

The influence of temperature was studied in order to know the kinetics of esterification. The reaction rate increased when the temperature was increased. The experimental results were found to fit a first-order kinetic law for the forward reaction and a second-order for the reverse reaction.

The influence of temperature was found to be insignificant on the transesterification reaction. Nevertheless, methanol/oil mole ratio influenced up to 6.0:1. The influence of upper mole ratios was insignificant on the FAME content evolution.

Based on the experimental results, biodiesel from used frying oil did not fulfil all the specifications from EN 14214 Standard due to the chemical modifications in the oil during cooking (presence of polar compounds). Therefore, biodiesel was proposed for use in combustion processes or in blends with biodiesel from other vegetable oils or even animal fats, which had not undergone chemical modifications.

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1. Introduction

Liquid biofuels are a growing and interesting alternative to petrol-based fuel because of the economic, environmental and supply problems of fossil fuels. Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and non-toxic, has low emission profiles and so is environmentally beneficial [1]. It is an advantageous option for the substitution or reduction of fossil fuel consumption. Biodiesel is defined, according to The American Society for Testing and Materials (ASTM), as monoalkyl esters of long chain fatty acids (FAME) derived from a renewable lipid feedstock, such as vegetable oil or animal fat [2].

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and alcohol to yield fatty acid alkyl esters (i.e. biodiesel) and glycerol as a by-product [2]. Methanol is the most commonly used alcohol because of its low cost and its physical-chemical advantages (polar compound and short chain alcohol). At

industrial scale, alkaline catalyst is the most used due to its suitable operational conditions: low cost, easy to install and, above all, its high reaction rate which provides a decrease in the equipment size and in immobilized capital.

The main disadvantage of using biodiesel is the high cost of the raw material, which leads to a very expensive final product in comparison with petrol-diesel. In recent years many studies have been carried out on biodiesel production from used frying oils [2–5] as well as the research of new vegetable species [6–9], all of them with a view to overcoming the economic barrier.

In this sense, used frying oils are a good raw material because of their low cost and the environmental advantage of the residue valorisation. Spain is a large vegetable oil consumer, mainly olive and sunflower oils; in addition, used frying oils do not undergo significant alterations and can be easily adapted as biofuel because they are unlikely to be reused.

Cooking is a dehydration process; it means that water and soluble compounds are transferred from fried food to oil. At the same time, fried products absorb a part of the surrounding oil. Edible oils are constantly exposed to chemical reaction during cooking, due to their composition and external influences. The reactions are led by oxygen, light and heat. Three main reactions take place: oxidation, polymerization and hydrolysis.

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Table 1
Chemical analysis of used frying oil and fatty acid profile (free and linked acids).

Test	Results (wt.%)	Test	Results (wt.%)
Polar compounds:	20.90	Triglycerides content	73.58
• FFA	2.14	Moisture	0.43
• Diglycerides content	1.97	Ash content	0.16
• Monoglycerides content	n/d		
• Other polar compounds ^a	16.79		
Fatty acid profile	%	Fatty acid profile	%
C14:0 Tetradecanoic (myristic)	0.19	C20:0 Eicosanoic (arachidic)	0.55
C16:0 Hexadecanoic (palmitic)	10.26	C20:1 Eicosenoic (gadoleic)	0.14
C18:0 Octadecanoic (stearic)	3.85	C22:0 Docosanoic (behenic)	0.65
C18:1 Octadecenoic (oleic)	47.83	C22:1 Docosenoic (erucic)	0.01
C18:2 Octadecadienoic (linoleic)	36.10	C24:0 Tetracosanoic (lignoceric)	0.04
C18:3 Octadecatrienoic (linolenic)	0.38		

^a Polimeric triglycerides and oxidized monomeric triglycerides

- Oxidation produces oil ageing due to contact with atmospheric oxygen. Oxidation is accelerated because of temperature and light. Triglycerides, which are present in oil, are oxidizable organic compounds. In fact, when the number of double bonds rises, oxidation takes place easily. As well as degraded products, oxidation produces hydroperoxides, aldehydes and ketones.
- Polymerization is a chemical reaction where unsaturated fatty acids - due to the influence of heat, heavy metals (Cu, Fe) or light and by means of the breakage of the double bond - reacts to form dimers (molecule composed of two identical subunits or monomers linked together) and polymers of triglycerides. As a consequence of polymerization, the oil molecular weight rises and the oil becomes more viscous.
- Hydrolysis is led by water acquisition in the fried product and is supported by certain products deep-fried in batter. Free fatty acids (FFAs) are generated because triglycerides are broken down. Moreover, when the water evaporates through the oil, monoglycerides, diglycerides and FFAs are created.

Thus, the new products formed during frying are polymers, dimers, oxidized triglycerides (hydroperoxides, aldehydes and ketones), as well as diglycerides and fatty acids [10]. So used frying oils are heterogeneous as compared to crude or refined oils. All these groups possess higher polarity that the initial triglycerides and can be easily quantified by means of adsorption chromatography [10–11] to find out the total degradation of frying oils.

Regarding the transesterification, it is found that crude oils (95% of triglycerides + partial glycerides) would give more than 98 wt.% of FAME in a complete conversion. However, in the case of used frying oils, non-altered FAME depend on the variable quality of the used frying oil [10]. At present, the determination of polar compounds can be applied in used frying oils and FAME obtained in order to know the real composition in biodiesel. In addition, Ruiz-Méndez et al. [10] proposed to study how polar compounds might interfere in the standard gas chromatographic determinations for evaluating the quality of biodiesel (EN 14103; EN 14105).

Due to the chemical reactions, the physical and chemical properties of the oil change during cooking [12]. A great deal of research has been conducted to characterize these physical and chemical changes [13–16]. As previously mentioned, the percentage of FFAs has been found to increase due to triglyceride hydrolysis in the presence of food moisture. For instance, the level of FFAs in fresh soybean oil went from 0.04 wt.% to 1.51 wt.% after 70 h of frying at 190 °C [12,16]. It was also observed that the acid value, specific gravity and saponification value of the used frying oil increased, but the iodine value decreased. The peroxide value increased to a maximum and then started to decrease [17].

The effectiveness of the alkaline transesterification process depends on the quality of the vegetable oil used for transesterification. Oil, containing a large quantity of free fatty acids, cannot be

directly used for biodiesel fuel production applying the commonly used alkaline transesterification procedure; free fatty acids have to be esterified before the transesterification of triglycerides can take place [18]. Canakci and Van Gerpen [19] recommend this pre-treatment since, if the FFA level exceeds 0.5 wt.%, saponification will hinder the separation of the ester from glycerine and reduce the yield and formation rate of FAME due to alkaline catalyst consumption. This is the case of used frying oils. So an esterification step is necessary before transesterification. This reaction is usually carried out in batch reactors with pressure and temperature conditions (ambient pressure and 60 °C) where the esterification reaction acts as the limiting step of the production. The aim of this work was to investigate the acidity removal and the subsequent transesterification at different temperatures and mole ratios in a batch reactor in order to improve the biodiesel production from used frying oils.

2. Materials and methods

The raw material utilized in this work was used frying oil (mainly olive and sunflower oil) from the refuse collection of the company BIDA, S.A. (Fuentes de Andalucía, Spain), with an acid value of 4.26 mg KOH.g⁻¹ oil (FFA level of 2.14 wt.%). Table 1 shows the most important characteristics of this used frying oil.

All the properties of the samples were analyzed according to the Standard Methods. The polar compound content (in used frying oil, esterified oil and biodiesel) was determined by a method in accordance with Standard Method 2507–IUPAC [11]. The non-polar FAME content was determined by a method in accordance with EN 14103 Standard [20]. The water content was determined by the Karl Fisher method (ISO 12937 Standard) [21] and the acid value was determined by titration with KOH in accordance with EN 14104 Standard [22]. The monoglyceride (MG), diglyceride (DG), triglyceride (TG) and free glycerol contents were determined by a method in accordance with EN 14105 Standard [23]. Kinematic viscosity and density were determined in accordance with ISO 3104 Standard [24] and ISO 3675 Standard [25] respectively. The iodine value was determined by a method in accordance with EN 14111 Standard [26].

Due to the chemical composition of used frying oil (Table 1), non-polar and polar FAME (oxidized monomeric FAME, dimeric FAME, and oligomeric FAME) were present in the biodiesel obtained.

The experimental set-up (Fig. 1) used for both esterification and transesterification was a batch stirring reactor close to the atmosphere. The device is composed of a stainless steel tank reactor (1 L capacity) with pressure and liquid phase temperature displays, where the heating system consisted of a jacketed reactor through which thermostated glycerol at the required temperature was circulated. Moreover, the system was made up of magnetic agitation,

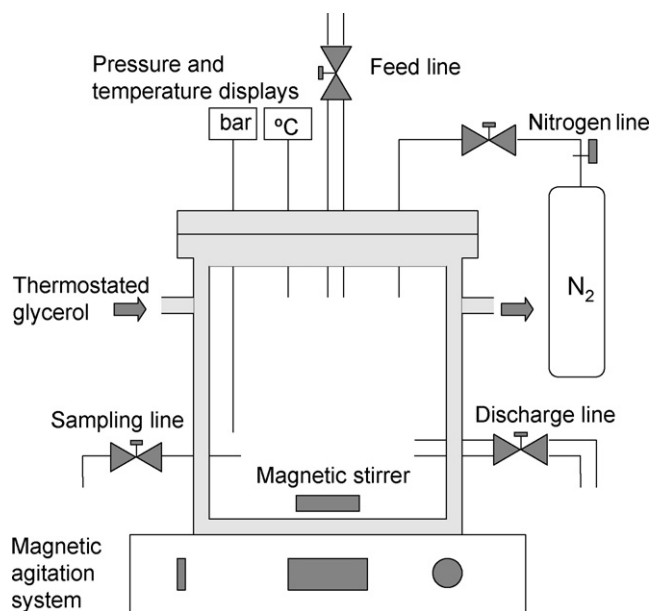


Fig. 1. Batch reactor experimental set-up.

which made it possible to control the agitation speed at the desired interval. During the tests, samples of 5 mL of liquid phase were withdrawn by using a line equipped with a stopping valve, similar to other used by Tesser et al. [27]. The system was charged with all the reactants and when the temperature was reached, the reaction time started.

In all the tests, 20% (0.2L) of the total volume was maintained as headspace in order to find out the methanol number of moles in the gas phase at each temperature. Given that the vapour pressure of methanol at 80 °C is 1.82 atm [28] and if the perfect gas equation is applied, the calculated methanol mole number would be 0.0126. This value was less than 0.5% approx. of the total amount of methanol in the liquid phase. Therefore, the methanol was in liquid phase only at selected conditions.

With the aim of finding out the consumed power when the number of revolutions of the stirrer is changed, the Reynolds number was calculated. For stirred tanks, the Reynolds number is calculated by the next expression:

$$Re_i = \frac{N_i \cdot D_i^2 \cdot \rho}{\mu} \quad (1)$$

where Re_i is the Reynolds number, N_i the number of revolutions of the stirrer, D_i the stirrer diameter, ρ the fluid density and μ the fluid dynamic viscosity.

For the used system, with the diameter of the stirrer at 2.5 cm, the agitation speed 600 rpm, the fluid density $0.915 \text{ g}\cdot\text{cm}^{-3}$ and the fluid dynamic viscosity $0.295 \text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}$, the Re_i was 194. Therefore, the flow was turbulent ($Re_i > 10$). Actually, during the initial stage, the Reynolds number controller is the oil dynamic viscosity and it grows as the fluid dynamic viscosity decreases so the turbulent flow increases with the FAME formation.

For systems in turbulent mode, the consumed power was calculated by Doran [29]:

$$P = N'_p \cdot \rho \cdot N_i^3 \cdot D_i^5 \quad (2)$$

where N' is a constant value of the power number in turbulent mode. Given that the power increases with the revolutions number cube, it is justified to work with the minimum value of N_i to avoid the reaction control by matter transfer.

In previous studies [2,30,31] similar esterification conditions were reported but only over ambient pressure conditions. Ester-

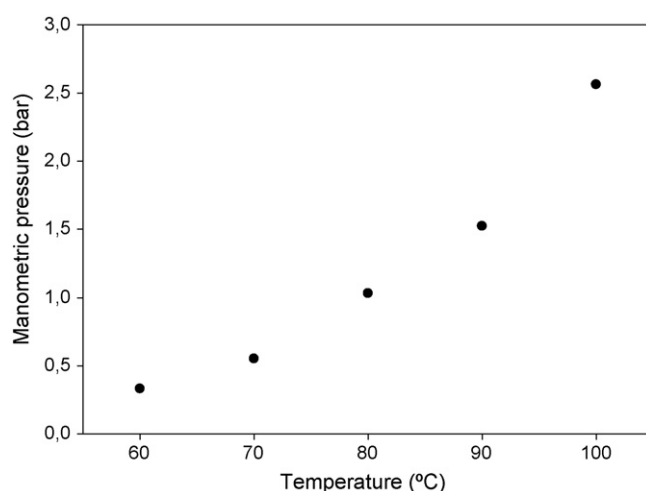


Fig. 2. Relation between temperature and manometric pressure in esterification experiments.

ification tests were carried out at 600 rpm (fixed speed in previous paper; [30]), H_2SO_4 as acid catalyst at concentration of 5 wt.% (relative to total acidity as oleic acid), using a methanol/oleic acid mole ratio of 60:1 and different temperatures (60, 70, 80, 90 and 100 °C). Fig. 2 depicts the relation between the temperature and the obtained manometric pressure.

The reaction development was checked by the acid value determination by means of the titration with KOH solution in accordance with the EN 14104 Standard [22]. Samples were taken from the reactor at several times and were then washed with deionised water in order to stop the reaction, centrifuged and dried under vacuum conditions to remove the washing water.

The used frying esterified oil, which has been utilized in the transesterification reaction, contains 9.6 wt.% FAME from a previous esterification (0.34 wt.% FFA content).

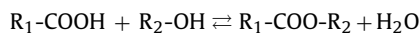
The transesterification conditions were taken from the background literature [3,32,33] and modified in order to study the influence of the temperature and excess methanol over the reaction. Transesterification tests were carried out at several temperatures (60, 70 and 80 °C), a methanol/oil mole ratio of 4.5:1, 6.0:1 and 7.5:1, 600 rpm and an alkaline catalyst concentration (KOH) of 1.0 wt.%.

The transesterification development has been checked by the determination of methyl esters content in a VARIAN 3900 GC by a method in agreement with the EN 14103 Standard [20]. Samples were taken from the reactor at several intervals and were then kept cold. The glycerol-phase was removed and the methyl ester-phase was washed with deionised water to remove impurities, then centrifuged and dried under vacuum conditions.

3. Results and discussion

3.1. Esterification

The elimination of FFAs relies on the well-known esterification reaction:



which is catalysed by acids. In this work, R_1 was a linear chain of 13–23 carbon atoms containing a variable number of unsaturations depending on the particular origin of the raw material, and R_2 was a methyl radical.

This reaction is heterogeneous (methanol is non-soluble in sunflower oil), so it requires agitation in order to avoid mass trans-

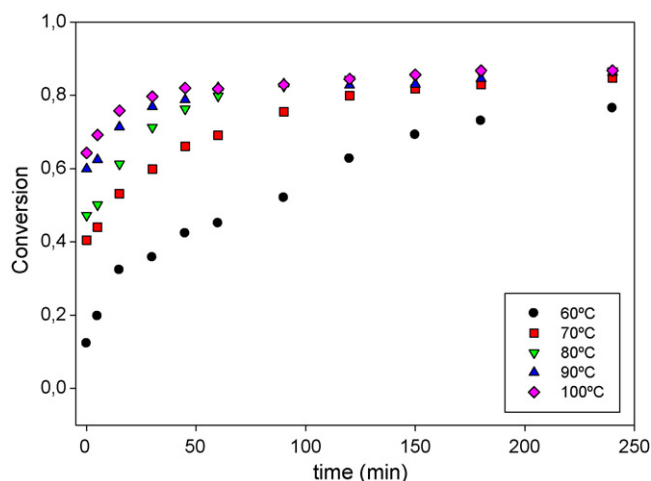


Fig. 3. Variation of the conversion of FFA to FAME at different temperatures (60, 70, 80, 90 and 100 °C). Methanol/oleic acid mole ratio of 60:1, H₂SO₄ concentration of 5 wt.% and agitation speed of 600 rpm.

Table 2
Characterization of esterified used frying oil.

Test	Results (wt.%)
Polar compounds:	25.20
• FFA content	0.34
• Diglycerides content	5.62
• Monoglycerides content	1.29
• Other polar compounds ^a	17.95
Non-polar FAME content	9.6
Triglycerides content	68.60
Moisture	0.39

^a Polimeric triglycerides and oxidized monomeric triglycerides

fer taking control of the process [1]. In this work, a speed of 600 rpm was used to examine the influence of the temperature on the conversion of FFA to FAME, because this value was found to have no further effect on the reaction rate in previous research [30].

The conversion was defined as the percentage of FFA converted to FAME. Fig. 3 shows the variation of the conversion of FFA to FAME at different temperatures (60, 70, 80, 90 and 100 °C) with each curve starting at the conversion value reached at the initial time (isothermal conditions). It was found that the reaction rate increased when the temperature rose. However, between 90 °C and 100 °C the increase of the conversion did not justify the higher temperature and the associated costs. In all the tests, the equilibrium of the reaction was observed. The temperature increase caused the decrease of oil viscosity, improving the contact between reactants. The reaction time to obtain oil, with an acid value below 1 mg KOH·g⁻¹ oil (FFA level of 0.5 wt.%) was reduced considerably. These improvements were possible thanks to the characteristics of the experimental set-up. In order to optimize the operational conditions, the kinetics of the reaction was studied.

Table 2 shows some chemical characteristics of esterified used frying oil, where it can be observed that the triglyceride content did not show any significant variation because the formation of FAME from triglycerides in the esterification reaction is slower than in the transesterification step. Thus, diglycerides and monoglycerides appeared from the breakage of triglycerides. However, the fatty acid content decreased up to the recommended value in the background literature. The increase of the polar compound percentage, between initial and esterified used frying oil, was as a result of the appearance of new monoglycerides and diglycerides from the partial breakage of triglycerides. Furthermore, other polar compounds

were maintained because the esterification conditions (65 °C and 2 h) were not very extreme.

3.1.1. Kinetic model

The kinetic model used in this work is based on the following assumptions:

- The esterification reaction was a reversible heterogeneous process during which the chemical reaction controlled the rate of the operating conditions.
- The rate of the non-catalyzed reaction was negligible in comparison to the catalyzed reaction.
- The chemical reaction occurred in the oil phase.
- The methanol/oleic acid mole ratio used was high enough for the methanol concentration to remain constant throughout the process.

These assumptions were proved in previous research [30]. Under these conditions, the reaction was assumed to be *pseudo*-homogeneous, first-order in the forward direction and second-order in the reverse direction, and hence conforming to the following kinetic law:

$$\frac{-d[A]}{dt} = k_1 \cdot [A] - k_2 \cdot [C] \cdot [D] \quad (3)$$

where [A] denotes the concentration of FFA in mg KOH·g⁻¹ oil (*i.e.* the acid value); [C] and [D] are the concentrations of FAME and water, respectively, formed during the reaction, both referred to one gram of oil; so k_1 and k_2 are the kinetic constants for the forward and reverse reaction, respectively.

Equation 3 can be transformed using the acid value conversion definition (X_A) in the following equation 4:

$$\frac{dX_A}{dt} = k_1 \cdot \left[(1 - X_A) - \left(\frac{1 - X_{Aeq}}{X^2} \right) \cdot X_A^2 \right] \quad (4)$$

where X_{Aeq} is the equilibrium conversion as the average of 70, 80, 90 and 100 °C tests due to the fact that equilibrium was reached in all of the tests obtaining similar equilibrium conversion values. So the mean value of $X_{Aeq} = 0.859$ has been utilized to transform equation 4 into equation 5 which is the way to calculate k_1 .

$$\frac{dX_A}{dt} = k_1 \cdot [1 - X_A - 0.191 \cdot X_A^2] \quad (5)$$

The kinetic model, equation 5, was solved by the differential method of Fourth Order Runge–Kutta with the Mathcad 14.0 ® mathematical software. The value of k_1 , which has been adopted as the solution, was achieved when the sum of the squares of the deviations between experimental and calculated values were at a minimum.

For example, the adjustment of the conversion at 80 °C is shown in Fig. 4. As can be seen, the modelled curve fits the calculated conversion from experimental acid value concentration perfectly.

The influence of temperature on the esterification reaction was evaluated through the Arrhenius equation by fitting k_1 to temperature:

$$k_1 = A \cdot \exp \left[\frac{-E}{R \cdot T} \right] \quad (6)$$

This is shown in Fig. 5, where the exponential relation was demonstrated. Both the frequency factor A and the energy of activation E were obtained by nonlinear regression, using the Mathcad 14.0 ® software. The results are shown in Table 3.

An activation energy of about 28.7 kJ·mol⁻¹ was found for the forward reaction, slightly lower than the values for similar reactive systems obtained by Tesser et al. [27] for free fatty acid (oleic acid) esterification, by Berrios et al. [30] for olive fatty acids distillate in

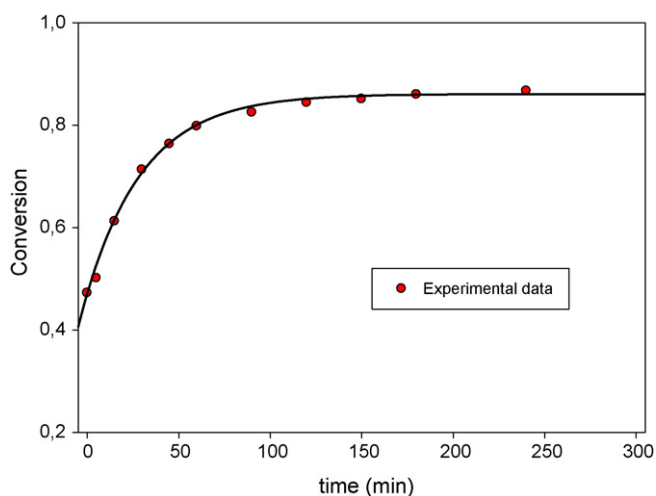


Fig. 4. Adjustment of the kinetic model selected to the experimental data at 80 °C.

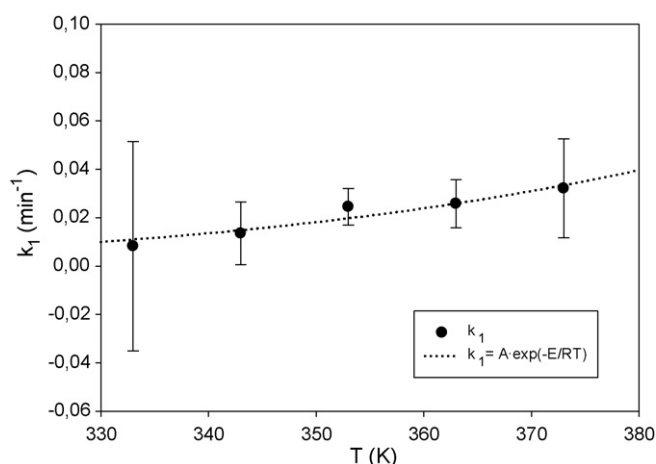


Fig. 5. Influence of temperature on the reaction rate (Arrhenius equation) at a H_2SO_4 concentration of 5 wt%, 600 rpm and 60:1 methanol/oleic acid mole ratio. Error bars indicate repeatability of the different measurements.

Table 3

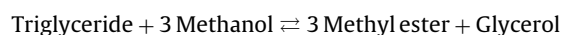
Energy of activation and frequency factor for the esterification of used frying oil.

	A (min^{-1})	E (J mol^{-1})	r
K_1	363	28693	0.95

sunflower oil esterification and by Aranda et al. [34] for palm fatty acid esterification. In contrast to these values, Sendzikiene et al. [18] showed activation energy around $13 \text{ kJ} \cdot \text{mol}^{-1}$ and laid down the assumption that diffusion restrictions were characteristic to the entire range of the concentrations and the reaction duration studied.

3.2. Transesterification

Just like the esterification reaction, transesterification is a heterogeneous reaction:



where the formation rate can be influenced by the agitation speed.

As it is well known, the catalyst used in the reaction influences the yield and the kinetics. As a consequence, there is a great deal of research into transesterification with different kinds of catalyst: alkaline, acid or enzymatic [33,35–38]. In this work, potassium

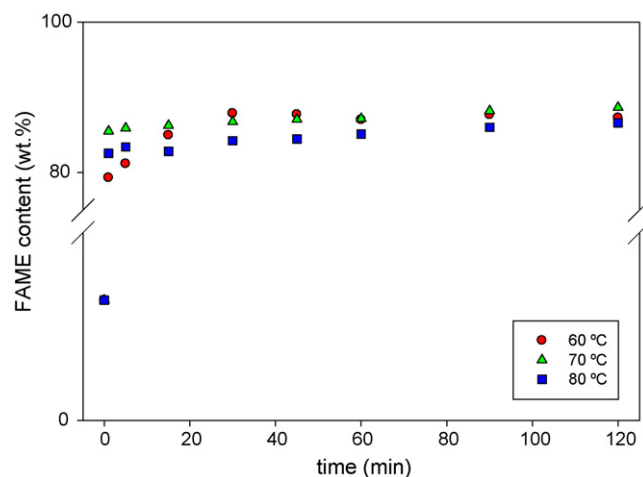


Fig. 6. Influence of the temperature on the evolution of the transesterification of used frying oil.

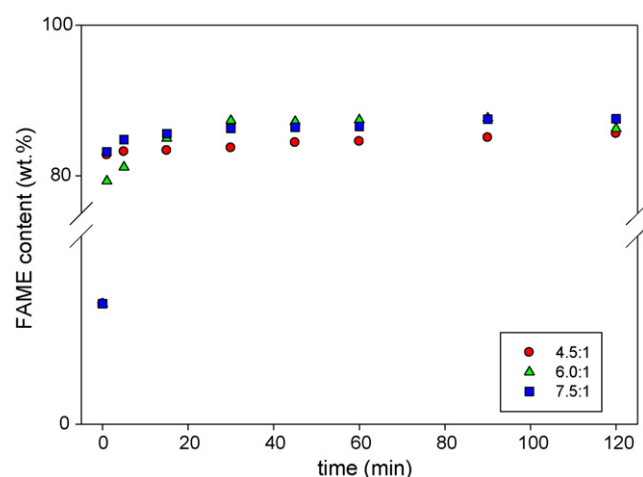


Fig. 7. Influence of methanol/oil mole ratio (4.5:1, 6.0:1 and 7.5:1) on the evolution of transesterification of used frying oil.

hydroxide was used as a process catalyst as it is the most used at industrial scale.

Fig. 6 shows the influence of temperature (60, 70 and 80 °C) on the evolution of the reaction when methanol/oil mole ratio was set at 6.0:1. It can be observed that temperature did not have a significant influence on the kinetics because the conversion to FAME happened quickly. In this way, workings over 60 °C did not improve the process.

Something similar happened when the influence of methanol/oil mole ratio was studied. Fig. 7 shows the influence of methanol/oil mole ratio (4.5:1, 6.0:1 and 7.5:1) on the evolution of the reaction at 60 °C. Although in the graph the differences are not detected, when a methanol/oil mole ratio of 4.5:1 was selected, the FAME content was almost constant and 2 wt.% lower than the other runs. So a methanol/oil ratio of 6.0:1 was selected as the most suitable amount of methanol.

The obtained product in the test with the most suitable conditions (600 rpm, 1.0 wt.% KOH, 6.0:1 methanol/oil mole ratio and 60 °C) was characterized by means of some of the EN 14214 Standard specifications. Table 4 shows these results, which do not fulfil all specifications from the standard.

Polar FAME was a direct measurement of thermoxidative degradation affecting unsaturated fatty acids [10]. The present polar compounds in this fraction were polymeric FAME and oxidized

Table 4
Characterization of obtained biodiesel from used frying oil in pressure system.

	Run	EN 14214	
		Minimum	Maximum
Acid value (mg KOH·g ⁻¹ oil)	0.14	-	0.50
Density at 25 °C (g·cm ⁻³)	0.875	0.860	0.900
Kinematic viscosity at 40 °C (mm ² ·s ⁻¹)	4.76	3.50	5.00
Iodine value (g I ₂ ·100 g ⁻¹ sample)	101.6		120
Non – polar FAME content (wt.%)	88.5	96.5	
Linolenic acid methyl ester content (wt.%)	0.6		12.0
Polar FAME content (wt.%)	7.4		
(Non – polar + polar FAME content) (wt.%)	95.9	96.5	

monomeric FAME. As compared to the polar compounds in the initial and esterified used frying oil, the polar compound percentage was much lower as it only included the modified fatty acyl groups in the triglyceride molecules (polar FAME). FFA, monoglycerides and diglycerides have been transformed to non-polar FAME during esterification and transesterification. According to Ruiz-Méndez et al. [10], there was a high correlation coefficient between polar compounds and polar FAME by means of the expression:

$$\text{Polar FAME}(\%) = 0.46 \cdot \text{Polar Compounds}(\%) - 1.4 \quad (R = 0.9768) \quad (7)$$

When the expression was applied to the polar compounds in the used frying oils, the expected polar FAME was 8.2%, which was 0.8% higher than the obtained result (7.4%). It can be deduced that the equation related the experimental data satisfactorily.

It is necessary to emphasize that the reaction did not reach the desired non-polar FAME content. If the polar FAME content was taken into account, the EN 14214 specification would be almost fulfilled: 95.9 wt.% (Table 4). The obtained biodiesel did not fulfil the FAME specification set out in the EN 14214 Standard due to the presence of polar compounds. Therefore, the polar FAME content must be considered in order to fulfil the ester content specification with used frying oils as raw material. So it is necessary before the transesterification process to carry out a complete characterization of used frying oils. Otherwise, used frying oils cannot be used to produce biodiesel with good quality parameters.

4. Conclusions

To obtain biodiesel from used frying oils (mainly olive and sunflower oils), it was necessary to carry out 2 steps: esterification and transesterification.

The acid value conversion was fitted satisfactorily to a kinetic model in accordance with a first order forward direction and second order in the reverse direction, plus the mean value of $X_{Aeq} = 0.859$.

The influence of temperature over the kinetics of esterification reaction was studied. The reaction rate increased when temperature rose. Obtaining the acid value below 1 mg KOH·g⁻¹ oil, an increase of temperature could be used in order to reduce reaction times. Increasing the temperature from 60 °C to 80 °C lead to the reaction rate being increased by 3.

Temperature had no significant influence on the evolution of transesterification reaction. The kinetics was so fast in the range selected than it is impossible to study with the available experimental set-up. Variations in the methanol/oil mole ratio showed a slight influence over the FAME content evolution. But to displace the forward reaction, it was necessary to use at least 6.0:1 methanol/oil mole ratio.

The non-polar FAME content was 88.5 wt.% according to the EN 14214 specification although it would be 95.9 wt.% including polar FAME content.

Acknowledgements

The authors are grateful to Ministry of Education and Science (MEC, Spain) for the PhD grant AP2005-3537 and the firm BIDA, S.A. for funding this work. The authors would like to thank the lab technician Inmaculada Bellido for her collaboration.

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