TRANSESTERIFICATION OF VEGETABLES OIL IN SUBCRITICAL METHANOL CONDITIONS

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ABSTRACT: In this study, transesterification of rapeseed oil using subcritical methanol and potassium hydroxide as catalyst was studied. The variables affecting the methyl ester yield during the transesterification reaction, such as the catalyst content, reaction temperature, reaction time and the molar ratio of alcohol to oil, were investigated. The results are compared to the obtained using co-solvents. The evolution of the process was followed by gas chromatography, determining the concentration of the methyl esters. The biodiesel was characterized by its density, viscosity, saponification value, iodine value, acidity index and water content, according to ISO norms. High methyl ester yield and fast reaction rate could be obtained even if the reaction pressure was relatively low, which is quite favourable to the production of biodiesel in industry.
Keywords: biodiesel, rapeseed oil, transesterification, methanol.

1 INTRODUCTION

By Directive 2003/30/EC, biodiesel is defined as "a methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel"[1]

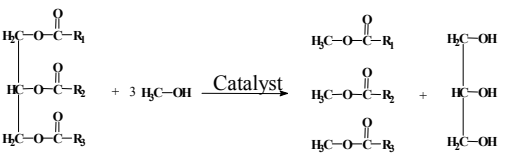
Nowadays, biodiesel, made from the oils of various types of oil seed crops like sunflower, palm, cottonseed, rapeseed, soybean and peanut has become very attractive as a biofuel because of its environmental benefits it has less air pollutants per net energy than diesel and is non-toxic and biodegradable and because it is produced from renewable sources with high energetic efficiency: biodiesel yields from an estimated 90% to 40% more energy than the energy invested in producing it. [2, 3]

One of the advantages of this fuel is that the raw materials used to produce it are natural and renewable. All these types of oils come from vegetables or animal fat, making it biodegradable and non-toxic. The typical fatty acid composition of rapeseed oil and their chemical properties, used in this work, are given in Table I. [4, 5]

Table I: Fatty acid composition (% by weight)

	6:1	**18:0**	**18:1**	**22:1**	**18:2**	**18:3**
Rapeseed oil	3.49	0.85	64.4	0.00	22.30	8.23

Today, most of the biodiesel is produced by the alkali-catalyzed process, such as transesterification. The simplified form of its chemical reaction is present in equation:



Trigliceride Methanol Methyl esters (biodiesel) Glycerol

In the transesterification of different types of oils, triglycerides react with an alcohol, generally methanol or ethanol, to produce esters and glycerol. To make it possible, a catalyst is added to the reaction. The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides diglyceride is obtained, from diglyceride monoglyceride is produced and in the last step, from monoglycerides glycerol is obtained. In all these reactions esters are produced. The stecheometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product. [6-8]

Transesterification of vegetable oils to biodiesel with methanol can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base and enzymatic) catalysts. Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts in transesterification.

When 1 wt.% NaOH (or KOH) is used, it often takes about 1 h to ensure the transesterification reaction to complete. However, in this conventional method, the removal of these catalysts is technically difficult. Moreover, in the alkaline-catalyzed process, soap formation would occur even if there is little water and fatty acid in the reactants. [9] It is, thus, of great interest from a practical point of view to study a practically possible process without using any catalyst or using a little amount as possible.

Saka and Kusdiana have firstly proposed that biodiesel may be prepared from vegetable oil via non-catalytic method with supercritical alcohol. [10]

Supercritical fluids (SCFs) are good solvents for many substances when compressed into its state of above the critical temperature and critical pressure. SCFs have both gaslike viscosities and liquidlike densities. They were obtained much more concerns in a lot of fields such as supercritical fluid extraction, reaction, materials formation and analysis. Compared with the traditional chemistry method, this novel method requires no catalyst and nearly complete conversions can be achieved in a very short time. So it successfully overcomes most problems in conventional chemical processes. However, the synthesis of biodiesel by supercritical methanol has drawback with high cost of apparatus due to the high temperature and pressure, which are not viable in the large practice in industry. Because supercritical methanol method has so many advantages, many researches have focus on how to improve the reaction conditions (such as shorten reaction time, decrease reaction temperature, and pressure). Co-solvent added to the reactant can decrease the operating temperature, pressure and the amount of

alcohol, such as carbon dioxide, hexane and calcium oxide. [11]

This study has aimed at the conversion of rapeseed oil to biodiesel via the transesterification reaction with potassium hydroxide (KOH) in subcritical methanol.

2 EXPERIMENTAL PROCEDURES AND METHODS

2.1 Materials

Rapeseed oil was provided by Research Center "The Order", Section of Non-Food Crops. Potassium hydroxide (KOH) was supplied by Merck (pellets GR for analysis). Methanol was purchased from Panreac (99% v/v). All other chemicals were obtained commercially and of analytical grade.

The oil studied was characterized, as table II.

Table II: Characterization of oils studied

	Density 15ºC (kg/m^3)	Viscosity 40ºC (cSt)	Iodine value ($g_{I2}/100g$)	Acid value (mg_{KOH}/g)
Rapessed oil	906.8	32.0	112.2	2.29

2.2 Reaction procedure

The subcritical methanol transesterification system employed in this work is shown in Fig. 1.

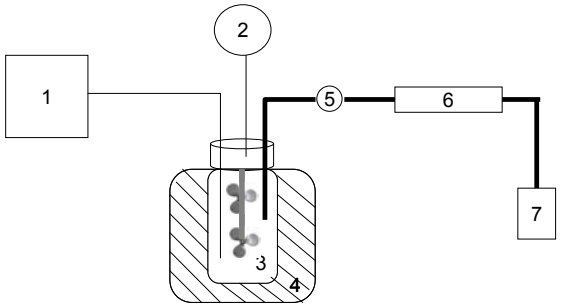


Figure 1: Subcritical methanol transesterification system: (1) temperature control monitor; (2) pressure monitor; (3) cylindrical vessel of teflon; (4) electrical furnace (cylindrical reactor made of stainless steel); (5) product exit valve, (6) condenser and (7) collecting samples.

A cylindrical reactor made of stainless steel, equipped with a magnetic stirrer and internal cooling system was used. The pressure and temperature were monitored in real time up to maximum values of 250 bar and 250ºC, respectively. Within the reactor is introduced a 300 mL cylindrical vessel of teflon. The reaction vessel was charged with a given amount of oil and a liquid solution of methanol and KOH, with different ratios. Then, the vessel was heated with an external heater, and the liquid solution was stirred at a constant rate at the same time. When the desired temperature was reached, the process remained for a set time. Then, after cooling, the steel reactor was opened, and the reaction vessel was removed. After that, the mixture was placed in the separatory funnel and allowed to ensure that the separation of the methyl esters and the glycerol phase occurred completely. The glycerol phase (bottom phase) was removed and left in a separate container. The methyl esters (biodiesel) were evaporated at 85ºC for 30 minutes. The remaining catalyst was extracted by successive rinses with distilled water. Finally, the water present was eliminated by heating at 110 °C.

Table III shows the conditions of the experiments in this work.

Table III: Experimental conditions

Exp.	MeOH:Oil	KOH (wt.%)	Temp. (ºC)	Reactor Pressure (bar)
1	6:1	1.0	100	2.0
2	9:1	1.0	100	2.0
3	9:1	0.7	100	2.0
4	9:1	0.5	100	2.0
5	12:1	1.0	100	2.0
6	12:1	0.7	100	2.0
7	12:1	0.5	100	2.0
8	12:1	0.3	100	2.0
9	12:1	1.0	150	10.0
10	24:1	1.0	100	2.0
11	24:1	1.0	150	10.0
12	24:1	0.5	150	10.0
13	24:1	0.1	150	10.0
14	24:1	1.0	180	20.0

2.3 Analytical methods

The methyl ester content was assayed by gas chromatography in a VARIAN 3900 chromatograph, provided with a FID, employing a silica capillary column of 30 m length, 0.32 mm ID, and 0.25 mm film thickness. Heptane was used as solvent, and the carrier gas was helium at a flow rate of 0.7 mL/min. The injector temperature was kept at 270 ºC, and the detector temperature, 300 ºC. Temperature ramp starting with 200 ºC, then 20 ºC/min up to 220 ºC.

The calibration curve of peak area and the quantity of biodiesel was linear.

The analytical methods used to determine the characteristics of the biodiesel are basically those recommended by the European Organization for Normalization (CEN). This organization specifies the criteria that should be satisfied by a biodiesel of high quality, or diesel and biodiesel mixtures, for its use in motor vehicles. [12]

3 RESULTS AND DISCUSION

The operation variables employed were ethanol/oil molar ratio (6:1–24:1), catalyst concentration (0.1–1.0 wt.%), temperature (100–180 °C). Reaction time (60 min), oil type (rapeseed), catalyst type (KOH) and alcohol type (methanol) were fixed as common parameters in all experiments.

3.1 Effect of reaction temperature on biodiesel yield

Temperature clearly influences the reaction and yield of the biodiesel product. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time. However, several authors found that when the reaction temperature increases beyond the optimal level, the yield

of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides. [8, 13, 14]

Fig. 2, phase diagram of methanol, shows the point where it becomes a supercritical fluid. In this study we worked down of these conditions, as shown in Table III.

Effects of the reaction temperature on the methyl ester yield are shown in Fig. 3.

The synthesis of biodiesel was conducted at various temperatures (100-180 ºC) at the fixed molar ratio of alcohol to oil of 24:1 and a fixed mass ratio of potassium hydroxide (KOH) of 1 wt%. Experimental results showed that the transesterification reaction could proceed within the temperature range studied and the reaction rate was lightly increased with the increase of the reaction temperature, from 100ºC to 150ºC. The same does not happen when the temperature increases to 180 ºC.

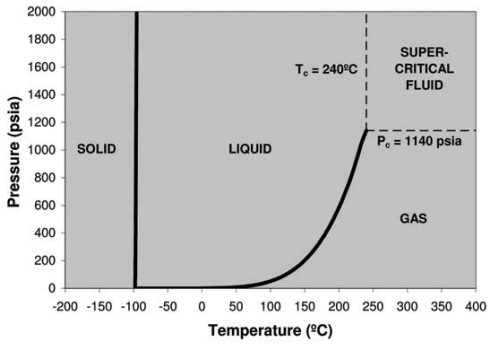


Figure 2: Phase diagram of methanol showing the point where it becomes a supercritical fluid [15]

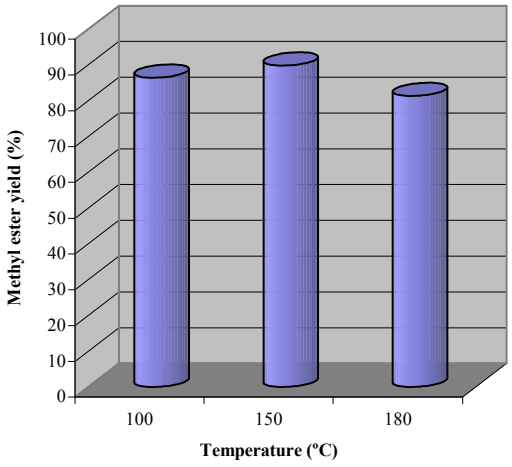


Figure 3: Effect of reaction temperature on biodiesel yield (1wt% KOH, molar ratio of methanol to oil: 24:1, reaction time: 60 min).

3.2 Effect of methanol/oil molar ratio on biodiesel yield

The biodiesel yield could be improved by introducing excess amounts of methanol to shift the equilibrium to the right-hand side. Further increasing the alcohol amount beyond the optimal ratio will not increase the yield but will increase cost for alcohol recovery.

The effect of alcohol amount on yield of the transesterification experiments was conducted with different ratios of methanol to oil in the range of 6:1 to 24:1. The reactions were carried out at a fixed potassium hydroxide (KOH) mass of 1.0 wt% and fixed reaction temperature of 100ºC. Fig. 4 shows the changes in percentage of methyl esters formed with the different molar ratios of methanol to oil. It can be seen that increasing the molar ratio of methanol to oil from 6:1 to 12:1, the methyl ester yield increased from 75.3% to close 98%. However, the yields were slightly reduced when the ratio of methanol to oil was higher than 12:1.

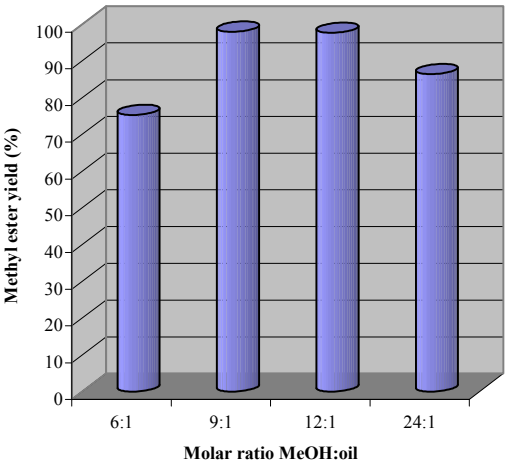


Figure 4: Effect of methanol/oil molar ratio on the yield (1wt% KOH, reaction temperature: 100ºC, reaction time: 60 min).

3.3 Effect of mass ratio of catalyst to oil on biodiesel yield

Catalyst concentration can affect the yield of the biodiesel product. As the catalyst concentration increases the conversion of triglyceride and the yield of biodiesel increase. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters. Usually, the yield reaches an optimal value when the catalyst concentration reaches 1.5 wt. % and then decreases a little with a further increase in catalyst concentration. The reduction of the yield of the biodiesel is due to the addition of excessive alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap. [8]

The amount of potassium hydroxide is very important for the reaction. First the cost of production depends on the raw materials, and then more catalyst will increase the complexity of separation of product.

Effects of mass ratio of catalyst to oil on the methyl ester yield are shown in Fig. 5. The synthesis of biodiesel was conducted with different mass ratios of KOH (0.3-1.0%) at fixed reaction temperature of 100ºC and for two molar ratios of alcohol to oil (9:1 and 12:1).

Experimental results showed that is possible achieve conversions above 90% for a small mass ratio of catalyst to oil.

3.4 Effect of reaction time on biodiesel yield

The conversion rate increases with reaction time. At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at a reaction time of <90 min, and then remains relatively constant with a further increase in the reaction time. Moreover, excess reaction time will lead to

a reduction in the product yield due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps. [8, 14, 16]

Effects of reaction time on the methyl ester yield are shown in Fig. 6. The timing was started when the reactor was closed, requiring only about 20 minutes to reach a temperature of 100 ºC. As can be observed, the behaviour is similar in all cases. There is an initial period in which the yield increases drastically, and a final period, more extended, once the equilibrium is reached. Apart from the experiment carried out to 30 ºC, the situation of equilibrium is reached in 20-30 minutes.

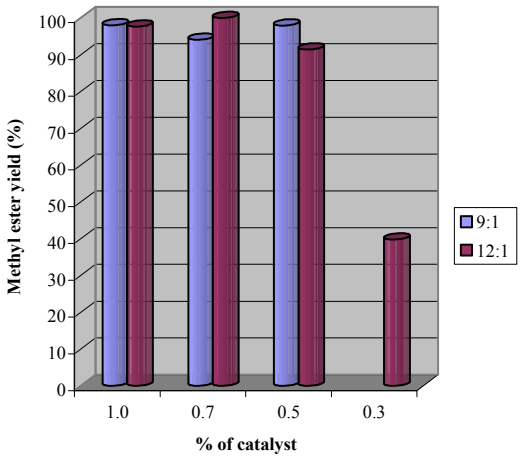


Figure 5: Effect of mass ratio of catalyst to oil on biodiesel yield (reaction temperature: 100ºC, reaction time: 60 min).

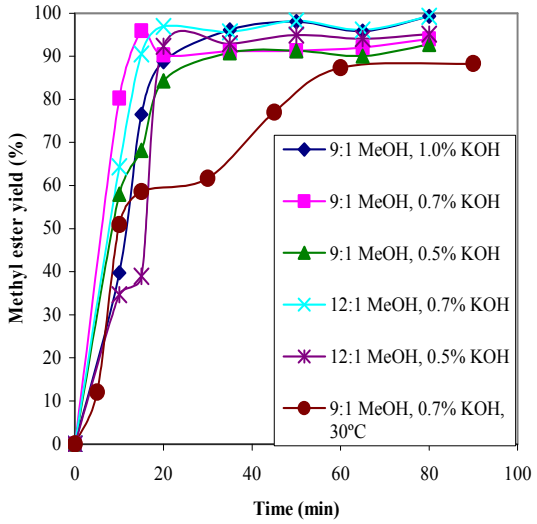


Figure 6: Effect of time reaction on biodiesel yield

3.5 Effect of co-solvent on biodiesel yield

Since the transesterification of vegetable oils with methanol is a two phase reaction system, the mass transfer between the two phases becomes a significant factor that affects the reaction rate. Thus, vigorous mechanical mixing and/or heating are necessary to improve the mass transfer across the boundary between the two phases, what is an energy-consumptive process.

Several authors reported that a methanol/oil two-phase system became homogeneous by addition of a co-solvent and thus the transesterification rate in the alkaline catalyst system rose drastically. [17, 18]

The effect of diethyl ether (DEE), used as co-solvent, on biodiesel yield are shown in Fig. 7. Experimental results show that the utilization of DEE as co-solvent has a similar effect to using subcritical methanol. Both allow achieved high biodiesel conversions in a short interval of time.

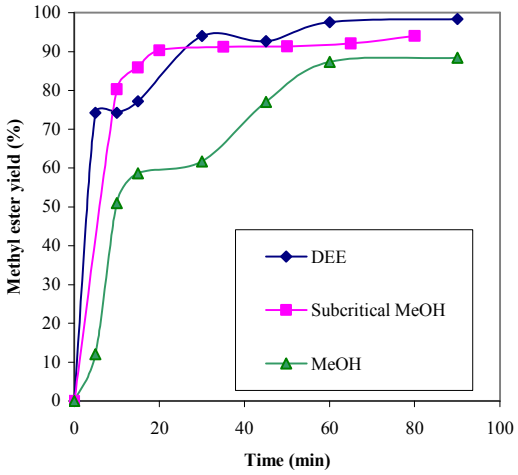


Figure 7: Effect of using DEE, as co-solvent, on biodiesel yield. ♦ DEE (0.7%KOH, 9:1MeOH, 30ºC, 700rpm, DEE: MeOH 1:1) ■ Subcritical MeOH (0.7%KOH, 9:1MeOH, 100ºC) ▲MeOH (0.7%KOH, 9:1MeOH, 30ºC, 700rpm)

3.6 Effect of oil type

In this work three different vegetables oils were compared, using subcritical methanol. As shown in Fig. 8, rapeseed oil has higher yields (99.9%). Nevertheless, the results obtained with the three types of oil are very similar. In consequence the utilization methanol in sub-critical conditions is positive in all cases.

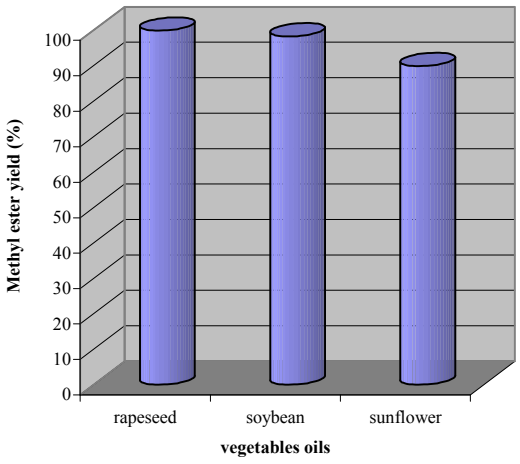


Figure 8: Effect of oil type on biodiesel yield

3.7 Fuel specifications

Tables IV-a, IV-b and IV-c show the influence of operating variables on the main parameters of biodiesel obtained in each experiment. These parameters are very important since the quality of final product (biodiesel) is strongly conditioned by them. The fuel properties of the biodiesel were determined with the help of standard tests, and it was found that the biodiesel properties were very close to diesel fuel specifications, according to EN-590, and biodiesel European Standard draft. For comparison, in Table IV-c, a column with standard EN-14214 values has been enclosed.

The density presents values between 862.7 and 901.6 $kg.m^{-3}$, which are practically in the values recommended by the standard EN-14214. As it can be seen in Table IV, the density remains practically constant because the methanol, oil and esters have very similar density. The value obtained for the experiments 8 and 13 are justified by the low yield.

The viscosity is a very important property related to the biodiesel utilization in direct injection diesel engines. High values of viscosity give rise to a poor fuel atomization, incomplete combustion, and carbon deposition on the injectors. Therefore, the biodiesel viscosity must be low. The value required by standard EN-14214, at a temperature of 40 °C, must range between 3.5 and 5.0 cSt. As it can be observed, in table IV, for experiments 8 and 13 the viscosity values obtained are well above the maximum allowed. The variables studied showed a similar behaviour; that is, as methyl esters yield increased, the viscosity decreased. In consequence, the viscosity, as the other properties, is related with the grade of conversion achieved, that is, depending on the final yield.

As it can be observed in Table IV, the saponification values ranged from 162.2 to 174.9 mg of KOH per gram of sample. The saponification value is related to the average molecular weight of the sample. But the acids that are present in the glycerides or in the methyl esters are the same. Only the change of glycerol by methanol is produced, in consequence the average molecular weight does not change significantly and, changes in the saponification value are not very observed.

The number of double bonds of fatty acids is related to the iodine value. This parameter describes the content of unsaturated fatty acids and is only dependent on the origin of the vegetable oil. In consequence, the biodiesel obtained from the same oil should have similar iodine values. In our case the iodine values ranged between 104.5 and 119.9. This dispersion can be attributable to the heterogeneity of the samples and to the dilution of these with ethanol but, in all cases, the iodine values indicated were inferior to the maximum iodine from the standard EN-14214, witch is 120. A limitation of unsaturated fatty acids may be necessary because the higher heating of unsaturated fatty acids results in polymerisation of glycerides. This can lead to the formation of deposits or to the deterioration of the lubricating oil. This effect increases with the number of double bonds in the fatty acid chain.

The acidity index, expressed as mg KOH/g of sample, is in accordance with the maximum required limits given in the EN-14214 biodiesel standard norm (0.5 mg KOH/g), except from biodiesel 8 and 13. In these experiments the value was above the limit, which is explained by the low yield achieved.

Table IV a: Biodiesel characterization

	Experiments					**EN-14214**
	1	**2**	**3**	**4**	**5**	
Methyl ester yield (%)	75.3	98.0	94.0	97.91	97.7	96.5
Density$_{15\,°C}$ ($kg.m^{-3}$)	881.4	864.0	870.4	862.7	870.8	860-900
Viscosity$_{40°C}$ (cSt)	6.0	4.7	4.7	4.7	4.6	3.5-5.0
Water content (%)	0.07	0.08	0.04	0.05	0.05	< 0.05
Saponification value (mg/g)	163.3	170.0	167.9	172.7	162.2	-
Iodine value (%)	109.4	117.7	119.9	122.2	108.0	≤ 120
Acidity index (mg KOH/g)	0.39	0.48	0.39	0.38	0.41	≤ 0.5

Table IV b: Biodiesel characterization

	Experiments					**EN-14214**
	6	**7**	**8**	**9**	**10**	
Methyl ester yield (%)	99.9	91.4	39.8	93.0	86.4	96.5
Density$_{15\,°C}$ ($kg.m^{-3}$)	871.1	869.1	891.4	873.5	874.4	860-900
Viscosity$_{40°C}$ (cSt)	4.5	5.4	16.1	4.8	4.8	3.5-5.0
Water content (%)	0.05	0.11	0.21	0.08	0.05	< 0.05
Saponification value (mg/g)	174.9	169.3	164.7	166.6	165.8	-
Iodine value (%)	116.7	119.6	113.9	109.3	106.8	≤ 120
Acidity index (mg KOH/g)	0.48	0.37	0.54	0.40	0.30	≤ 0.5

Table IV c: Biodiesel characterization

	Experiments				**EN-14214**
	11	**12**	**13**	**14**	
Methyl ester yield (%)	89.8	90.1	21.3	81.3	96.5
Density$_{15\,°C}$ ($kg.m^{-3}$)	864.8	871.7	901.6	879.6	860-900
Viscosity$_{40°C}$ (cSt)	4.7	4.8	24.3	5.5	3.5-5.0
Water content (%)	0.09	0.08	0.12	0.19	< 0.05
Saponification value (mg/g)	166.9	164.0	165.9	168.3	-
Iodine value (%)	107.8	104.5	111.0	105.6	≤ 120
Acidity index (mg KOH/g)	0.37	0.36	1.32	0.45	≤ 0.5

4 CONCLUSIONS

In this study, we intended to coupling the base catalysis with the subcritical methanol, for biodiesel synthesis, from vegetable oils.

A small amount of KOH was an excellent catalyst in the transesterification reaction at subcritical temperatures, where soap formation did not occur. The main factors affecting the methyl ester yield during the

transesterification reaction were the catalyst content, the reaction temperature, and the molar ratio of oil to alcohol. High methyl ester yield and fast reaction rate could be obtained even if the reaction pressure was relatively low, which is quite favourable to the production of biodiesel in industry.

It was obtained a biodiesel yield of 99.9% when using a reaction temperature of 100ºC, a molar ratio of methanol to oil 12:1 and mass ratio of catalyst to oil of 0.7%.

The fuel properties of the biodiesel were determined with the help of standard tests, and it was found that the biodiesel properties were very close to diesel fuel specifications, according to EN-590, and EN-14214.

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