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Influence of fatty acid composition of raw materials on biodiesel properties

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ABSTRACT

The aim of this work was the study of the influence of the raw material composition on biodiesel quality, using a transesterification reaction. Thus, ten refined vegetable oils were transesterificated using potassium methoxide as catalyst and standard reaction conditions (reaction time, 1 h; weight of catalyst, 1 wt.% of initial oil weight; molar ratio methanol/oil, 6/1; reaction temperature, 60 °C). Biodiesel quality was tested according to the standard [UNE-EN 14214, 2003. Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods]. Some critical parameters like oxidation stability, cetane number, iodine value and cold filter plugging point were correlated with the methyl ester composition of each biodiesel, according to two parameters: degree of unsaturation and long chain saturated factor. Finally, a triangular graph based on the composition in monounsaturated, polyunsaturated and saturated methyl esters was built in order to predict the critical parameters of European standard for whatever biodiesel, known its composition.

1. Introduction

The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). However, these sources are limited, and will be exhausted by the near future (Dermibas, 2005). Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. This fuel is biodegradable and non-toxic and has low emission profiles as compared to petroleum diesel. Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment (Meher et al., 2006). Recently, the demand of biodiesel has increased due to petroleum price rises in the last few months and the development of government measures like the EU Directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport (Vicente et al., 2007).

Biodiesel, is produced through a reaction known as transesterification. In a transesterification or alcoholysis reaction, one mole of triglyceride reacts with three moles of alcohol (molar ratio of methanol to vegetable oil of 3:1) to form one mole of glycerol and three moles of the respective fatty acid alkyl esters. The process is a sequence of three reversible reactions, in which the triglyceride molecule is converted step by step into diglyceride, monoglyceride and glycerol (Mittelbach and Remschmidt, 2004).

Several reviews dealing with the production of biodiesel by transesterification have been published (Dermibas, 2005; Fukuda et al., 2001; Ma and Hanna, 1999; Schuchardt et al., 1998). Generally, transesterification can proceed by base or acid catalysis. However, in homogeneous catalysis, alkali catalysis (sodium or potassium hydroxide; or the corresponding alkoxides) is a much more rapid process than acid catalysis (Freedman et al., 1984).

Several types of vegetable oils, with a varied composition in fatty acids, can be used for the preparation of biodiesel. Four oil crops clearly dominate the feedstock sources used for world-wide biodiesel production. Soybean (Sensöz and Kaynar, 2006; Xie et al., 2006), rapeseed (Cvengros and Povazanec, 1996; Peterson et al., 1996), palm (Kalam and Masjuki, 2002) and sunflower (Antolín et al., 2002; Vicente et al., 2005) oils are the most studied. However, there are no technical restrictions to the use of other types of vegetable oils. Often the vegetable oils investigated for their suitability as biodiesel are those which occur abundantly in a specific area. Thus, Spain, along with France and Italy, is one of the major world producers of grape seed oil, obtained from the seeds left following pressing of the juice from grapes for wine making. Biodiesel production from grape seed oil constitutes an economic alternative for valuation of by-product obtained from the wine manufacture in the region of Castilla-La Mancha (Spain).

Vicente et al. (2006) examined the methanolysis of 21 different vegetable oils to produce biodiesel in Spain, including traditional vegetable seed oils (sunflower and rapeseed), alternative vegetable oils (*Brassica carinata*), genetically modified vegetable oils (high oleic sunflower), and used frying oils.

The properties of the triglyceride and the biodiesel fuel are determined by the amounts of each fatty acid that are present in the molecules. Chain length and number of double bonds determine the physical characteristics of both fatty acids and triglycerides (Mittelbach and Remschmidt, 2004). Transesterification does

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not alter the fatty acid composition of the feedstocks and this composition plays an important role in some critical parameters of the biodiesel, as cetane number and cold flow properties.

Studies about the influence of the triglycerides composition in the biodiesel quality are scarce. Muniyappa et al. (1996) reported density, viscosity and cloud point of two biodiesels synthesized by soybean and beef tallow oil. The high cloud point of methyl esters from beef tallow oil was indicative of a high concentration of saturated fatty esters. Lang et al. (2001) tested several oils (rapeseed, sunflower, canola and linseed oil) on the biodiesel production and compared some physical and fuel properties of biodiesels with those of conventional diesel fuels. Cardone et al. (2003) reported a comparison of the performance of *B. carinata* oil-derived biodiesel with a commercial biodiesel and petroleum diesel fuel. This study was centred in the oxidation stability on the basis of linolenic acid content. Dmytryshyn et al. (2004) performed the transesterification of four vegetable oils, comparing properties like density, viscosity, cloud point and pour point, and establishing differences between them. Sarin et al. (2007) reported some blends of biodiesel from Jatropha and Palm oils to study their physico-chemical properties in order to improve the oxidation stability.

The main purpose of this work is based on the study of the influence of vegetable oils properties and composition on the quality of biodiesel synthesized. It has been reported the transesterification of common oils (rapeseed, soybean, sunflower and palm oil) and others less investigated as olive, almond, corn, grape seed and high oleic sunflower oil. The fatty acid profile of vegetable oils used was measured following the International and European Standards ISO 5509 and EN 14103. The quality of the biodiesels synthesized was tested according to the European Standard EN 14214. Relations between the composition of vegetable oils and critical parameters of biodiesel were obtained allowing us to predict some critical parameters in the biodiesel knowing the composition of the raw material.

2. Methods

2.1. Materials

Refined palm, olive, peanut, rape, soybean, sunflower and almond oil were provided by FLUKA. Refined grape seed oil was supplied by BORGES. Refined high oleic sunflower (HOS) was obtained from a local store and, finally, refined corn oil from SIGMA. Anhydrous methanol (99.8%) and acetic acid were obtained from PANREAC. The catalyst (potassium methoxide) was 97% purity from BASF. The following chemicals were supplied by FLUKA: heptane (puriss. p.a., $\geqslant$99.5% GC); methyl heptadecanoate (puriss. p.a., standard for GC, $\geqslant$99.7%). The following chemicals were supplied by SUPELCO: tricaprin (8000 μg/mL in pyridine); 1,2,4-butanetriol (1000 μg/mL in pyridine); monoolein (5000 μg/mL in pyridine); diolein (5000 μg/mL in pyridine); triolein (5000 μg/mL in pyridine); standard FAME mix (Supelco 37). *N*-Methyl-*N*-(trimethylsilyl)trifluoroacetamide (derivatization grade) and glycerol (meets USP testing specifications) were obtained from Sigma–Aldrich Chemical Company. Potassium hydroxide aqueous solution (0.1 N), ethanol 96%, diethyl ether was provided by PANREAC for the determination of the acid value. The following chemicals were necessary for the measure of iodine value and were supplied by PANREAC: cyclohexane, Wij's reagent, sodium thiosulphate ethanolic solution (0.1 N) and potassium iodide was supplied by PANREAC.

2.2. Equipment

Transesterification experiments were carried out in a 200 mL four-necked batch reactor. The reactor was equipped with a reflux condenser, to avoid methanol losses, a magnetic stirrer, a thermocouple connected to a heater plate to temperature control, and two stoppers to remove samples and to feed the raw materials, respectively.

2.3. Experimental procedure

The reactor was initially charged with the oil and preheated to the desired temperature. The catalyst (potassium methoxide) was dissolved in the methanol and the resulting solution was added to the agitated reactor. The reaction was timed as soon as the catalyst and methanol solution was added to the reactor. After the prefixed time, the reaction was immediately quenched with the stoichiometric amount of acetic acid to neutralize the catalyst. Then, the mixture was three-times washed with deionised water, and subsequently was centrifuged to remove the aqueous layer compound by methanol, residual catalyst and glycerol. The residual methanol and water were separated from biodiesel portion via rotary evaporation under vacuum at 80 °C during 1 h. Finally, a molecular sieve (3A) was added to each sample to adsorb the trace amount of moisture. Samples were stored under −17 °C until analysis.

2.4. Analytical methods

The composition and quantity of methyl ester in biodiesel was determined according to biodiesel test method UNE-EN 14103, using a HP 6890 series 2 gas chromatograph with a flame ionization detector. The capillary column was a DB-WAX column with a length of 30 m, a film thickness of 0.25 μm and an internal diameter of 0.32 mm. Helium was used as carrier gas and also as an auxiliary gas for the FID. One micro-litre of sample was injected using a 6890 Agilent Series Injector (Knothe et al., 2005).

The fatty acid profile of the vegetable oils was measured following the International and European Standards ISO 5509 (to prepare the methyl esters) and EN 14103 (to measure the methyl esters profile), using the same chromatograph described previously.

Methanol content was measured according to UNE-EN 14110, using the same apparatus as that described for the methyl ester content. The capillary column was a DB-1 column with a length of 30 m, a film thickness of 3 μm and an internal diameter of 0.32 mm. Samples was injected automatically using a 7694E Agilent Headspace Sample.

Trimethylsilylation of glycerol, mono- and diglycerides, followed by gas chromatography using a 15 m capillary column coated with a 0.1 μm film of DB-5HT allows the determination of all analytes in a GC run (Plank and Lorbeer, 1995). For the quantitative determination of free glycerol, mono-, di- and triglycerides, a calibration with the reference substances glycerol, mono-, di- and triolein as well as two internal standards (1,2,4-butanetriol and tricaprin) was carried out. This procedure was developed according to UNE-EN 14105.

Acid value or neutralization number, is expressed in mg KOH required to neutralize 1 g of fatty acid methyl esters and is set to a maximum value of $\leqslant$0.5 mg KOH/g in the European norm (EN 14214). The procedure involves titration of the diluted sample with ethanolic potassium hydroxide solution using a Metrohm 702 SM Titrino. This procedure was developed according to UNE-EN 14104.

The viscosity of biodiesel is about an order of magnitude lower than that of the parent oil and depends on the composition of alkyl esters. Kinematic viscosity was measured with a Canon–Fenske capillary viscosimeter immersed in a constant temperature (40 °C) bath (TAMSON TV 2000) following the European norm EN ISO 3104.

The flash point method uses a closed-cup flash point tester Stanhope Seta series 3 (ISO 3679) and serves to restrict the amount

of alcohol in the biodiesel fuel to a maximum of about 0.1% in the biodiesel fuel.

Both ASTM D 6751 and EN 14214 specify methods using a cetane engine, an engine specially modified for testing cetane number. Some equations correlate cetane number with the composition of biodiesel. In this case, it was necessary to use literature data for the fatty acid ester composition for the fuel used in testing the property equation (Mittelbach and Remschmidt, 2004). In this work, the correlation formulated by Clements (1996) was used obtaining a good correlation between reported and predicted biodiesel cetane numbers. Cetane number for biodiesels was predicted using Eq. (1):

$$\mathrm{CN} = \sum X_{\mathrm{ME}}(\mathrm{wt.\%}) \cdot \mathrm{CN}_{\mathrm{ME}} \quad (1)$$

where CN, is the cetane number of the biodiesel, X_{ME} is the weight percentage of each methyl ester and CN_{ME} is the cetane number of individual methyl ester.

Oxidative stability expresses the susceptibility to oxidation upon exposure to air of biodiesel (Dunn, 2005). Metrohm 743 Rancimat was used to determinate the induction period. This procedure was developed according to EN 14112.

Iodine value was measured by titration in a Metrohm 702 SM Titrino following the European standard EN 14111.

Cold filter plugging point (CFPP) test calls for cooling a FAME sample at a specified rate and drawing it under vacuum through a wire mesh filter screen. CFPP is then defined as the lowest temperature at which 20 mL of sample safely passes through the filter within 60 s (European norm EN 116). An automatic tester ISL FPP 5Gs was used to carry out the determination of the CFPP (Knothe, 2006; Knothe et al., 2005).

3. Results and discussion

The fatty acid profile of the vegetable oils used in this work is summarized in Table 1. There are three main types of fatty acids that can be present in a triglyceride: saturated (Cn:0), monounsaturated (Cn:1) and polyunsaturated with two or three double bonds (Cn:2,3). The percentage of these compounds for each vegetable oil is given in Table 2. According to this composition, two parameters based on the type of fatty acids were defined: degree of unsaturation (DU) and long chain saturated factor (LCSF). Both parameters are shown in Table 2.

Degree of unsaturation parameter was obtained from the empirical Eq. (1), taking into account the amount of monounsaturated and polyunsaturated fatty acids (wt.%) present in the vegetable oil

$$\mathrm{DU} = (\text{monounsaturated Cn} : 1,\ \mathrm{wt.\%}) + 2 \cdot (\text{polyunsaturated Cn} : 2,3,\ \mathrm{wt.\%}) \quad (2)$$

Long Chain Saturated Factor (A), parameter was calculated from the composition of saturated fatty acids and their corresponding melting point ($\mathrm{MP_{Cn}}$) by using Eq. (3).

$$\mathrm{LCSF(A)} = \mathrm{MP_{C18}} \cdot \mathrm{C18(wt.\%)} + \mathrm{MP_{C20}} \cdot \mathrm{C20(wt.\%)} + \mathrm{MP_{C22}} \cdot \mathrm{C22(wt.\%)} + \mathrm{MP_{C24}} \cdot \mathrm{C24(wt.\%)} \quad (3)$$

Long Chain Saturated Factor (B), parameter was obtained from the empirical Eq. (4), taking into account the composition of saturated fatty acids and lending more weight to the composition of fatty acids with a long chain.

$$\mathrm{LCSF(B)} = 0.1 \cdot \mathrm{C16(wt.\%)} + 0.5 \cdot \mathrm{C18(wt.\%)} + 1 \cdot \mathrm{C20(wt.\%)} + 1.5 \cdot \mathrm{C22(wt.\%)} + 2 \cdot \mathrm{C24(wt.\%)} \quad (4)$$

The quality of the biodiesels synthesized was tested according to the European Standard EN 14214. In Table 3, European Standard parameters for biodiesels synthesized from the vegetable oils are given. Most of the parameters satisfied the limits imposed by the standard EN 14214. The degree of compliance of these parameters (ester content, methanol content, kinematic viscosity, acid value, triglycerides, diglycerides, monoglycerides and glycerol content -free and total- and flash point) depends on the degree of oil

Table 1
Fatty acid compositions (wt.%) of vegetable oils

Fatty acid		Palm	Olive	Peanut	Rape	Soybean	Sunflower	Grape	H.O. Sunflower	Almond	Corn
Lauric	C12:0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Myristic	C14:0	0.7	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Palmitic	C16:0	36.7	11.6	8.0	4.9	11.3	6.2	6.9	4.6	10.4	6.5
Palmitoleic	C16:1	0.1	1.0	0.0	0.0	0.1	0.1	0.1	0.1	0.5	0.6
Stearic	C18:0	6.6	3.1	1.8	1.6	3.6	3.7	4.0	3.4	2.9	1.4
Oleic	C18:1	46.1	75.0	53.3	33.0	24.9	25.2	19.0	62.8	77.1	65.6
Linoleic	C18:2	8.6	7.8	28.4	20.4	53.0	63.1	69.1	27.5	7.6	25.2
Linolenic	C18:3	0.3	0.6	0.3	7.9	6.1	0.2	0.3	0.1	0.8	0.1
Arachidic	C20:0	0.4	0.3	0.9	0.0	0.3	0.3	0.3	0.3	0.3	0.1
Gadoleic	C20:1	0.2	0.0	2.4	9.3	0.3	0.2	0.0	0.0	0.0	0.1
Behenic	C22:0	0.1	0.1	3.0	0.0	0.0	0.7	0.0	0.7	0.1	0.0
Erucic	C22:1	0.0	0.0	0.0	23.0	0.3	0.1	0.0	0.0	0.0	0.1
Lignoceric	C24:0	0.1	0.5	1.8	0.0	0.1	0.2	0.0	0.3	0.2	0.1
Nervonic	C24:1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0

Table 2
Composition (wt.%), degree of unsaturation (DU) and long chain saturated factor (LCSF)

	Palm	Olive	Peanut	Rape	Soybean	Sunflower	Grape	H.O. Sunflower	Almond	Corn
Saturated	44.7	15.7	15.6	6.5	15.3	11.1	11.3	9.3	13.9	8.0
Monounsaturated	46.4	76.0	55.7	65.3	25.6	25.6	19.1	62.9	78.0	66.4
Polyunsaturated (2,3)	8.9	8.4	28.7	28.3	59.1	63.3	69.4	27.6	8.4	25.3
DU	64.2	92.7	113.1	121.9	143.8	152.2	157.8	118.2	94.8	117.0
LCSF (A)[a]	2.9	1.7	3.8	0.6	1.6	2.1	1.7	2.0	1.4	0.6
LCSF (B)[b]	7.7	4.2	10.7	1.3	3.4	4.2	3.0	4.1	3.3	1.5

[a] Long chain saturated factor calculated using the melting point.
[b] Long chain saturated factor calculated using the methyl ester composition.

Table 3
Properties of biodiesel from all vegetable oils (UNE-EN 14214)

Property	Units	Test method	Limits		Palm	Olive	Peanut	Rape	Soybean	Sunflower	Grape	H.O. Sunflower	Almond	Corn
			Min.	Max.										
Ester content	wt.%	EN 14103	96.5		97.7	99.0	99.5	99.5	96.9	97.2	97.8	99.5	99.7	99.8
Kinematic viscosity, 40 °C	mm^2/s	EN ISO 3104	3.5	5.0	4.5	4.5	4.6	4.4	4.2	4.2	4.1	4.4	4.2	4.4
Flash point	°C	EN ISO 3679	120		176	178	176	170	171	177	175	174	172	170
Cetane number	–	–[a]	51		61	57	53	55	49	50	48	53	57	53
Oxidative stability, 110 °C	h	EN 14112	6.0		4.0	3.3	2.0	2.0	1.3	0.8	0.5	1.2	3.0	1.2
Acid value	mg KOH/g	EN 14104		0.50	0.12	0.13	0.10	0.16	0.14	0.15	0.27	0.21	0.17	0.15
Iodine value	g I_2/100 g	EN 14111		120[b]	57	84	97	109	128	132	138	102	92	101
Linolenic acid content	wt.%	EN 14103		12.0	0.2	0.6	0.3	7.9	6.3	0.2	0.4	0.1	0.8	0.1
CFPP	°C	EN 116		–[c]	10	−6	17	−10	−5	−3	−6	−6	−6	−12
Methanol content	wt.%	EN 14110		0.20	0	0	0	0	0	0	0	0	0	0
Monoglycerides content	wt.%	EN 14105		0.80	0.17	0.67	0.32	0.41	0.21	0.37	0.28	0.31	0.27	0.40
Diglycerides content	wt.%	EN 14105		0.20	0.06	0.09	0.07	0.08	0.10	0.07	0.08	0.05	0.08	0.06
Triglycerides content	wt.%	EN 14105		0.20	0.04	0.03	0.03	0.03	0.07	0.04	0.03	0.06	0.02	0.03
Free glycerol	wt.%	EN 14105		0.02	0.01	0.00	0.01	0.01	0.07	0.00	0.00	0.00	0.00	0.00
Total glycerol	wt.%	EN 14105		0.25	0.06	0.19	0.11	0.09	0.00	0.11	0.09	0.13	0.07	0.09

[a] Internal procedure.
[b] RD 61/2006 (Spain) iodine value, 140 max. (g I_2/100 g).
[c] RD 61/2006 (Spain) CFPP, 0 °C max. in summer time and −10 °C max in winter time.

refinement (previous pre-treatment step), the transesterification process (conversion) and the quality of phases purification step. However, some of these parameters were out of specification. These critic parameters depend on oil nature and were cetane number, oxidation stability, iodine value and cold filter plugging point. The limit for each parameter is shown in Table 3.

3.1. Cetane number

Cetane number (CN) is widely used as diesel fuel quality parameter related to the ignition delay time and combustion quality. Higher the cetane number is, better it is in its ignition properties (Meher et al., 2006). An adequate cetane number is required for good engine performance. High cetane numbers help ensure good cold start properties and minimize the formation of white smoke. Cetane number is measured by matching against the blends two reference fuels namely *n*-cetane and α-methylnaphthalene. It is not always possible to carry out engine tests to determine cetane number because of the cost of the reference fuels and the more effort required. Hence, there have been many attempts to calculate the cetane number. This work takes an approach to estimate the cetane number of biodiesels, being estimated for blend of methyl esters, according to Eq. (1). The predicted cetane numbers are shown in Table 3.

It is well known that biodiesel cetane number depends on the feedstock used for its production. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the cetane number (Bajpai and Tyagi, 2006; Dermibas, 2005; Knothe et al., 1998). Fig. 1 shows the correlation between the cetane number and the degree of unsaturation (Table 2). It is clear that the cetane number fits linearly with the degree of unsaturation. The cetane number for biodiesel should be a minimum of 51 (UNE-EN 14214). According to this, biodiesels of soybean, sunflower and grape seed oil were out of specification. Therefore, a higher degree of unsaturation than 137 make oils did not meet the European Standard for the cetane number. Low cetane numbers have been associated with more highly unsaturated components such as the esters of linoleic (C18:2) and linolenic (C18:3) acids (Knothe et al., 2003). Polyunsaturated fuels that contain high levels of C18:2 and C18:3 fatty acids include soybean, sunflower and grape seed oils (Table 1).

According to Knothe et al. (2003), high cetane numbers were observed for esters of saturated fatty acids such as palmitic (C16:0) and stearic (C18:0) acids. Palm biodiesel, rich in these

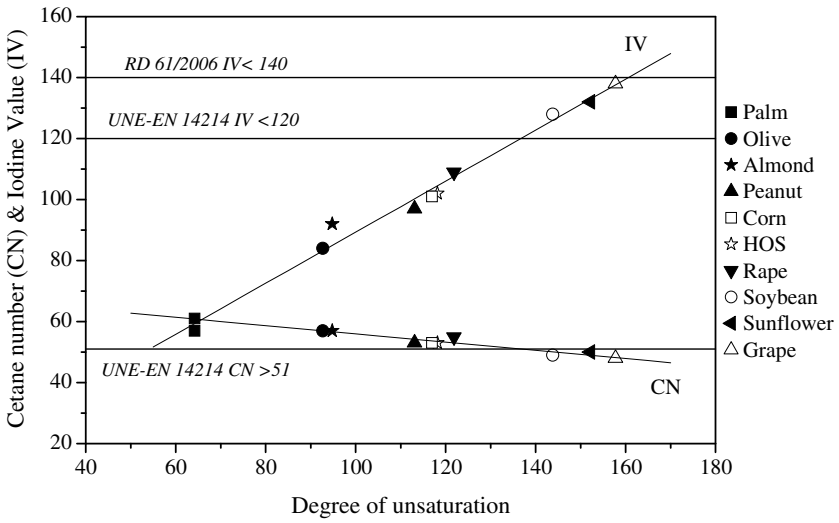

Fig. 1. Cetane number and iodine value of biodiesels versus the degree of unsaturation.

compounds (Table 1), gave the highest cetane number. Similar results were reported by Van Gerpen (1996) observing an increase of the cetane number with increasing the percentage of methyl palmitate in a blend.

Olive, almond and rapeseed biodiesels presented a cetane number near to palm biodiesel. These biodiesels are rich in monounsaturated compounds (Table 1): C18:1 the two former and C18:1, C20:1 and C22:1 the latter. The presence of these monounsaturated compounds gave a high cetane number to the biodiesels. In addition, the presence of long fatty acid carbon chain in rapeseed biodiesel led to a high cetane number for this biodiesel (Bajpai and Tyagi, 2006; Dermibas, 2005; Knothe et al., 1998).

Finally, peanut, high oleic sunflower and corn biodiesels, those which were richer in unsaturated ester of linoleic acid (C18:2), presents a cetane number in the medium range (Van Gerpen, 1996).

3.2. Iodine value

Iodine value is a measure of total unsaturation within a mixture of fatty acid. It is expressed in grams of iodine which react with 100 g of the respective sample when formally adding iodine to the double bonds. The iodine value of a vegetable oil or animal fat is almost identical to that of the corresponding methyl esters (Knothe et al., 2005).

Iodine value is limited to 120 g I_2/100 g in the European biodiesel standard UNE-EN 14214 (Table 3). The limit of 120 g I_2/100 g demanded by the European biodiesel standard excludes several promising oil sources such as soybean or sunflower seed oil, as well as grape seed oil, from serving as raw materials for biodiesel production (Mittelbach and Remschmidt, 2004). In Spain, the Royal Decree 61/2006 demands the completion of the European biodiesel standard UNE-EN 14214 except for the iodine value that changes from 120 to 140. According to this Spanish Royal Decree, all of vegetable oils satisfied the limit for the iodine value (Table 3). The limitation of unsaturated fatty acids is necessary due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits or to deterioration of the lubricating (Mittelbach, 1996).

The correlation between the iodine value and the degree of unsaturation (DU) is given in Fig. 1. As the iodine value is a measure of total unsaturation of a fatty material, a linear increases with the parameter DU was expected: the more unsaturation is present in the oil, the higher the iodine value (Knothe, 2002; Knothe et al., 1997; Kyriakidis and Katsiloulis, 2000; Lin et al., 2006).

Soybean, sunflower and grape seed oil were located between the limit imposed by the European Standard and the limit imposed by the Spanish law. These vegetable oils meet the linolenic acid methyl ester content (C18:3) imposed by the standard UNE-EN 14214 (max. 12.0 wt.%), however the content in linoleic acid methyl ester, with two double bonds in the carbon chain, was very high. Therefore, a higher degree of unsaturation than 137 make oils did not meet the European Standard for the iodine value. In Spain, the maximum degree of unsaturation is 160.

On the other hand, palm oil, rich in esters of saturated fatty acids such as palmitic (C16:0) and stearic (C18:0) acids, was the oil with a lower iodine value.

3.3. Oxidation stability

Oxidation stability is one of the major issues affecting the use of biodiesel because of its content of polyunsaturated methyl esters (Knothe, 2006). A minimum Rancimat induction period of six hours is defined for biodiesel samples within UNE-EN 14214 (Table 3). This limit corresponds to the period of time passing before fatty acid methyl esters, aged at 110 °C under a constant air stream, are degraded to such an extent that the formation of volatile acids can be recorded through an conductivity increase. It is well known that it is very difficult to meet this limit for biodiesel fuels derived from many common raw materials, unless antioxidants are added to the biodiesel. All the biodiesels obtained did not achieve the minimum limit of six hours for oxidation stability (Table 3). One feasible solution for increasing resistance of biodiesels against autoxidation is to treat them with oxidation inhibitors (antioxidants) (Rodríguez et al., 2006).

Stability of fatty compounds is influenced by factors such as presence of air, heat, traces of metal, peroxides, light, or structural features of the compounds themselves, mainly the presence of double bonds (Bajpai and Tyagi, 2006). The oxidation stability decreased with the increase of the contents of polyunsaturated methyl esters. Similar results were obtained by different authors (Knothe, 2005; McCormick et al., 2007; Park et al., 2008).

Autoxidation of unsaturated fatty compounds proceeds with different rates depending on the number and position of double bonds. The bis-allylic positions in common polyunsaturated fatty acids such as linoleic acid (one bis-allylic position at C-11) and linolenic acid (two bis-allylic positions at C-11 and C-14) are more susceptible to autoxidation than allylic positions. Relative rates of oxidation given in the literature are 1 for methyl oleate, 41 for methyl linoleate and 98 for methyl linolenate (Knothe, 2005; Knothe et al., 2005).

Therefore, vegetable oils rich in linoleic and linolenic acids, such as soybean, sunflower and grape seed oil (Table 2), tend to give methyl ester fuels with poor oxidation stability, whereas non polyunsaturated fuels, such as palm, olive and almond oil methyl esters, generally show improved stability.

3.4. Cold filter plugging point

Distillate fuels typically develop operability problems such as wax settling and plugging of filters and fuel lines when overnight temperatures approach −10 and −15 °C (Dunn and Bagby, 1996). The EN 14214 standard does not mention a low-temperature parameter in its list of specifications; however, it discusses the use of a low-temperature filterability test, the cold filter plugging point (CFPP). Each country using UNE-EN 14214 can specify certain temperature limits for different times of year depending on climate conditions (Knothe, 2006).

Table 3 shows the CFPP for all biodiesels synthesized. Palm biodiesel had poor low-temperature flow properties (10 °C of CFPP). If liquid biodiesel is cooled, the methyl esters of stearic and palmitic acid are the first amount to precipitate and therefore typically constitute a major share of material recovered from clogged biodiesel fuel filters (Mittelbach and Remschmidt, 2004). Palm biodiesel, rich in these compounds (Table 1), presents one of the highest CFPP.

Peanut biodiesel gave the worst CFPP (17 °C of CFPP). The bad low-temperature properties of peanut biodiesel have been tested by other authors (Wu et al., 2005). Peanut biodiesel is rich in methyl esters of long carbon chain saturated fatty acids like behenic (C22:0) and lignoceric (C24:0) acid (Table 1). The longer the carbon chains in the biodiesel, the worse the low-temperature properties (Wu et al., 2005).

Low-temperature properties depend mostly on the saturated ester content and the effect of unsaturated ester composition can be considered negligible (González-Gómez et al., 2002; Imahara et al., 2006). In this sense, the CFPP of the biodiesels was correlated with the parameter long chain saturated factor, LCSF(A), which was calculated using the melting point of the saturated fatty acid esters (Table 2, Eq. (3)). The unsaturated esters were not included in this parameter because the melting points of these compounds are

much lower compared with that of the saturated ones. In fact, unsaturated compounds act essentially as solvents, in which the saturated esters are dissolved and from which they precipitate by effect of the temperature (Lopes et al., 2008).

The correlation between CFPP and the parameter LCSF(A) is shown in Fig. 2. CFPP values increased with the parameter LCSF(A) and follows the Eq. (5):

$$\mathrm{CFPP} = 8.9243 \cdot \mathrm{LCSF(A)} - 19.325 \quad (5)$$

The correlation coefficient (R^2) was 0.8971.

In order to improve the prediction of the CFPP, this parameter was correlated with the LCSF(B), given in Table 2, calculated using only the composition in saturated methyl esters (Eq. (3)). The correlation between the CFPP and the saturated methyl ester content was obtained from Fig. 2 as follows:

$$\mathrm{CFPP} = 3.1417 \cdot \mathrm{LCSF(B)} - 16.477 \quad (6)$$

The better correlation of both parameters using Eq. (6) was tested by the highest correlation coefficient, $R^2 = 0.966$. From these results, it is possible to directly predict the CFPP of biodiesels from the content of saturated methyl esters, given more weight to those with longer carbon chain. The limits imposed in Spain for the CFPP are presented in Fig. 2. In Spain, a country of mild weather, a degree B (0 °C) in summer and a degree D (−10 °C) in winter time are specified.

3.5. Predicting biodiesel properties by methyl ester composition

The biodiesels synthesized using all vegetable oils tested in this work were represented in a triangular graph (Fig. 3) where the three angular points of the triangle meant the 100% of monounsaturated, polyunsaturated (2,3) and saturated methyl ester composition, respectively. The aim was to group together those biodiesel with similar properties given by similar methyl ester compositions.

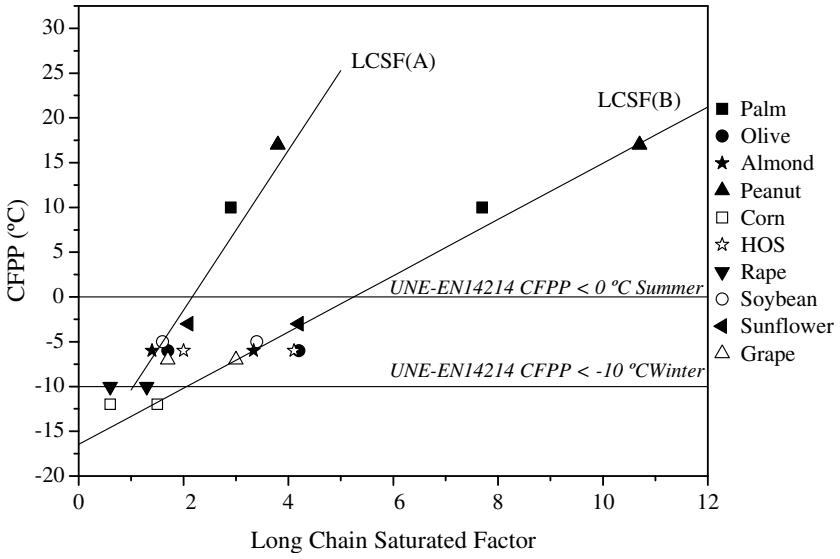

Fig. 2. Cold filter plugging point of biodiesel versus LCSF(A) and LCSF(B).

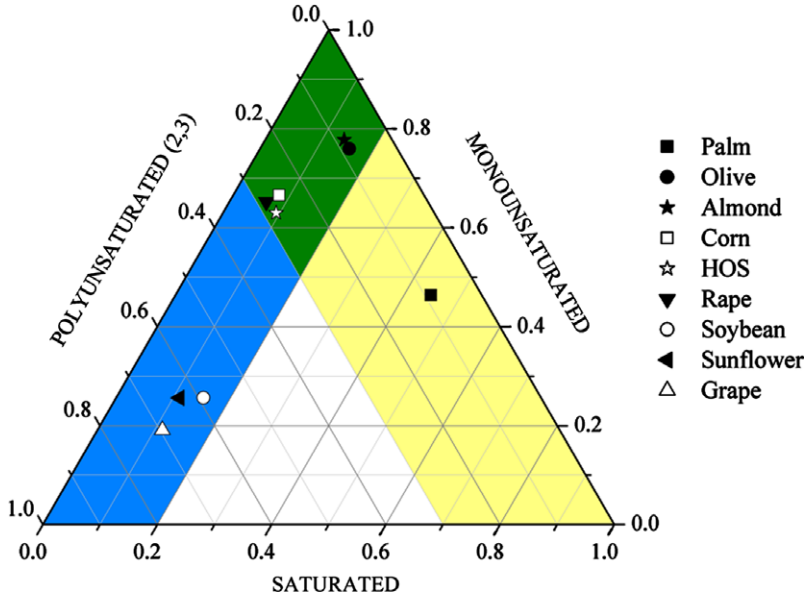

Fig. 3. Biodiesels by monounsaturated, polyunsaturated and saturated methyl esters. Areas satisfying parameter of the European Standard UNE-EN 14214: yellow (right), good cetane number and iodine value; blue (left), good CFPP; green (intersection), biodiesel that satisfied UNE-EN 14214.

In the triangular graph (Fig. 3), area which satisfies the limit of cetane number and iodine value existed at the far end of the polyunsaturated angular point (yellow area), having low content of polyunsaturated and high content of saturated methyl esters. This area corresponds to palm, olive, rape, high oleic sunflower, almond and corn biodiesels. All these biodiesel have a monounsaturated methyl ester composition higher than 50 wt.%. Sunflower, soybean and grape seed biodiesels, with high concentration on polyunsaturated methyl ester and low concentration on saturated ones, were out of this area.

On the other hand, area which satisfies the limit of cold filter plugging point parameter existed at the far end of the saturated angular point (blue area), having low content of saturated methyl esters. All biodiesels except palm one belong to this area. Peanut biodiesel was not considered for this classification because, as mentioned above, peanut did not meet the specification of CFPP because of the presence of long carbon chain saturated methyl ester and the length of the carbon chain was not included in the triangle. For all biodiesels belonging to this area, the monounsaturated methyl ester content was in the range of 20–80 wt.%.

If we superpose both areas, we found an optimum concentration area where biodiesels satisfied the limits imposed by UNE-EN 14214 for critical parameters like cetane number, iodine value and CFPP (green area). This area was characterized by a high concentration of monounsaturated fatty acids (like oleic acid, C18:1). Thus, almond, olive, corn, rapeseed and high oleic sunflower biodiesels, rich in monounsaturated compounds, were in this area. Therefore, monounsaturated fatty acid methyl esters such as methyl oleate is considered to be better than polyunsaturated ones such as methyl linoleate and methyl linolenate for cetane number and iodine value without any adverse effect on biodiesel cold properties (Imahara et al., 2006).

In Spain, the Communitarian Agrarian Policy (PAC) foments the high oleic sunflower and rapeseed production. This is favourable considering our results, because biodiesel of both vegetable oils were in the optimum concentration area allowing to obtain a biodiesel of good quality.

4. Conclusions

The main purpose of this work was based on the study of the influence of fatty acid composition of vegetable oils on the quality of biodiesel synthesized. Low cetane numbers have been associated with more highly unsaturated components (C18:2 and C18:3). Polyunsaturated fuels that contain high levels of these components include soybean, sunflower and grape seed oils. In addition, these biodiesels showed high iodine values. Furthermore, the oxidation stability decreased with the increase of the content of polyunsaturated methyl esters. This was not the case for the cold filter plugging point: biodiesels rich in long carbon chain saturated methyl esters showed the worst CFPP values. Biodiesel of almond, olive, corn, rapeseed and high oleic sunflower oils had the global better properties because they have the greater monounsaturated content.

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