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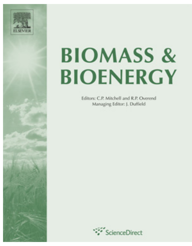

Fuel properties of biodiesel from vegetable oils and oil mixtures. Influence of methyl esters distribution

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ABSTRACT

In this work, the quality of biodiesel produced by basic transesterification from several vegetable oils (soybean, rapeseed, sunflower, high oleic sunflower, *Cynara Cardunculus L.*, *Brassica Carinata* and *Jatropha Curca*) cultivated in Extremadura has been studied in detail. The influence of raw material composition on properties such as density, viscosity, cetane number, higher heating value, iodine and saponification values and cold filter plugging point has been verified. Other biodiesel properties such as acid value, water content and flash and combustion points were more dependent on characteristics of production process. Biodiesel produced by rapeseed, sunflower and high oleic sunflower oils transesterification have been biofuels with better properties according to Norm EN 14214. Finally, it has been tested that it is possible to use oils mixtures in biodiesel production in order to improve the biodiesel quality. In addition, with the same process conditions and knowing properties of biodiesel from pure oils; for biodiesel from oils mixtures, its methyl esters content, and therefore properties dependent this content can be predicted from a simple mathematical equation proposed in this work.

1. Introduction

Biodiesel, a biofuel comprised in general of long-chain fatty acid methyl esters (FAMEs) derived from vegetable oils or animal fats, is an alternative to fossil fuels and it can also be used as a fuel additive. The advantages of biodiesel fuels over diesel fuel are well known (less smoke and particulates production, higher cetane number, domestic origin, lower carbon monoxide and hydrocarbon emissions. They also are biodegradable and non-toxic, and provide engine lubricity to low sulfur diesel [1–3]).

The most common route to biodiesel production is the transesterification reaction, shown in equation (1). This process involves several critical parameters which strongly influence the final yield, such as reaction temperature, alcohol/oil molar ratio, type of catalyst, type/chemical structure of alcohol, amount/concentration of catalyst, reaction time and other technical aspects (heating system, super-critical and sub-critical conditions, bath or continuous flow processes, etc.) [4–6].

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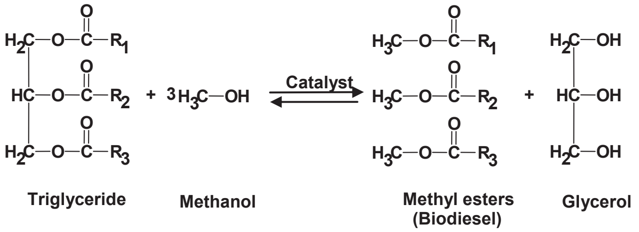

(1)

In addition to these factors, the selection of raw material is essential for the production of biofuel and this depends on local availability and corresponding affordability. Do not forget that the high production cost of biodiesel is largely attributed to the cost of feedstock. Traditionally, the use of edible vegetable oils and animal fats is the most widespread for biodiesel production. However, this use is controversial because edible vegetable oils compete with food materials – the food versus fuel dispute [7,8]. Therefore, recent focus about the use of non-edible plant oil source as the raw material for biodiesel production is on the rise: *Cynara Cardunculus L.* oil [9–11], *Jatropha Curcas L.* oil [12], *Brassica Carinata* oil [13,14], or *Pongamia Pinnata* oil [15]. Besides as European standard specification EN 14214 in 2004 defined the biodiesel as FAMEs from any kind of raw materials, including recycled frying oils, under fulfilling the given quality specifications; biodiesel production from used frying oils has also been studied in detail [3,16,17].

On the other hand, biodiesel quality depends on their fatty acid ester composition and therefore on fatty acid of raw materials (oils or fats). The main structural features that influence the physical fuel properties are chain length, degree of unsaturation and branching of the chain. Among the fuel specifications which depend on chemical composition are cetane number (CN), kinematic viscosity, density, oxidative stability, cold-flow properties in the form of cloud point (CP), pour point (PP), and cold filter plugging point (CFPP), iodine and saponification values (IV and SV), exhaust emissions, lubricity, and heat of combustion [7,18,19].

Therefore, the biodiesel production with full compliance with EN 14214 (or ASTM 6751-07) is a very challenging task. The search for new and low cost raw materials includes mixtures of different sources [20], as well as the development of simulation tools capable of predicting the properties of the final products [21].

According to these considerations, the main objective of this study is to determine the properties of different biofuels from vegetable oils (edible and not-edible) produced in the region of Extremadura (Spain) to check the influence of physical characteristics of these oils on the quality of biodiesel. The determined properties of biodiesel will be studied in detail. Also, different mixtures of oils with the best properties will be employed to improve the quality of biodiesel, as far as possible.

2. Materials and methods

2.1. *Materials*

Soybean (S), rapeseed (R), sunflower (SU), high oleic sunflower (HO), *Cynara Cardunculus L.* (CC), *Brassica Carinata* (BC), and *Jatropha Curca L.* (JC) oils were provided by Investigation Centre "*La Orden*" (Badajoz, Spain), Section of Non-Food Crops. Methanol (99.6 v/v%), potassium hydroxide (85 wt.%), sodium hydroxide (99 wt.%) and potassium methoxide (90 wt.%) were purchased from Sigma–Aldrich, Merck, Panreac and Alfa Aesar, respectively. Methyl esters of miristic, palmitic, palmitoleic, stearic, oleic, linoleic, linolenic, and erucic acids (employed as standards in the chromatographic determination) were purchased from Fluka and Sigma; and methyl heptadecanoate (used as internal standard) was purchased from Fluka. All reagents used in biodiesel characterization were of analytical grade. Moreover, mixtures of oils at different proportions by weight were also prepared for biodiesel production: rapeseed and soybean oils (50R50S; 75R25S; 25R75S), rapeseed and high oleic sunflower oils (50R50HO; 75R25HO; 25R75HO), and rapeseed, soybean and high oleic sunflower oils (33R33S33HO).

2.2. *Experimental procedure*

Transesterification reaction was carried out in a 500 mL spherical glass reactor, provided with a thermostat, magnetic stirring, condensation system, and sampling outlet. This installation was similar to that employed in previous works [9,22,23]. Before reactions, the material was washed and completely dried.

First, 250 g of vegetable oil or mixture were heated in the reactor at the reaction temperature, and when it was reached, methanol and dissolved catalyst were added and stirring started (zero time). At spaced intervals, samples of 2 mL were taken out from the reaction mixture and its methyl esters content was determined. Samples and reaction final mixture were placed in decantation funnels and allowed to stand overnight to ensure the complete phase separation (methyl esters and glycerol). The glycerol phase (bottom phase) was removed and the biodiesel phase (upper phase) was washed with deionizer water to reach neutral pH, to remove non-reacted methanol, homogeneous catalyst and possible glycerol remainders.

2.3. *Analytical procedure*

Biodiesel quality was evaluated according to biodiesel European Standard EN 14214. 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 [24]. Similar methods were used to characterize the vegetable oils.

The content and the composition of FAMEs were analyzed by gas chromatography (GC) in a VARIAN 3900 chromatograph, provided with a flame ionization detector (FID), using a silica capillary column Agilent Technologies 1909-BD-113 of 30 m length, 0.32 mm inner diameter, and 0.25 μm film thickness. Helium was used as carrier gas at a flow rate of 0.7 mL min^{-1}. Injector temperature was kept at 270 °C, and FID temperature at 300 °C. The oven was maintained initially at 200 °C, during 21 min, and then it was elevated to 220 °C, at 20 °C min^{-1} and remained for 10 min up to 220 °C. The fatty acid profile in vegetable oils was determined by GC: oils were transesterified according to ISO 5509:2000, the FAMEs were

Table 1 – Properties and fatty acids content of vegetable oils.

Parameter	Soybean (S)	Rapeseed (R)	Sunflower (SU)	High oleic sunflower (HO)	*Cynara Cardunculus* (CC)	*Brassica Carinata* (BC)	*Jatropha Curcas* (JC)
Density 15 °C, g L^{-1}	920.3	919.3	918.3	918.6	923.7	918.7	921.0
Kinematic viscosity 40 °C, cSt	39.3	38.5	38.3	38.0	37.5	41.4	39.0
Water content, wt.%	0.07	0.06	0.06	0.07	0.07	0.07	0.10
Acid value, mg$_{KOH}$·g$_{oil}^{-1}$	2.74	0.71	1.90	4.14	2.06	2.77	10.13
Iodine value, g$_{I2}$·100g$_{oil}^{-1}$	119.8	101.1	93.5	84.4	115.2	106.6	96.4
Saponification mg$_{KOH}$·g$_{oil}^{-1}$	193.2	184.0	187.7	185.1	190.1	188.3	190.8
Calculated[a] molecular weight, g mol^{-1}	847	908	879	871	866	868	797
Content of fatty acid, wt.%							
Miristic acid (C14:0)	0.09	0.07	0.05	0.03	0.12	0.06	0.07
Palmitic acid (C16:0)	11.60	4.92	4.88	3.92	8.96	3.90	13.95
Palmitoleic acid (C16:1)	0.11	0.24	0.11	0.18	0.23	0.29	1.07
Stearic acid (C18:0)	3.25	1.63	4.78	2.59	2.63	1.22	7.94
Oleic acid (C18:1)	25.09	66.59	67.66	85.31	27.65	24.18	42.71
Linoleic acid (C18:2)	52.93	17.08	21.26	6.71	45.04	19.79	33.78
Linolenic acid (C18:3)	5.95	7.75	0.09	0.05	4.09	13.18	0.05
Erucic acid (C22:1)	0.43	0.31	0.94	0.88	10.33	36.00	0.19
Others	0.56	1.40	0.33	0.33	0.95	1.39	0.23

[a] Calculation using acid value and saponification value.

analyzed by GC, identifying each FAME by comparison with standards, and quantifying from the peak areas.

The rest of determined properties were: density at 15 °C (pycnometry), kinematic viscosity at 40 °C (capillary viscosimeter, ISO 3104:1994), cetane number (CN) (cetane number prediction with its FAMEs composition according to Tong et al. [25]), unsaturation degree (UD) (unsaturation degree prediction with its FAMEs composition according to Ramos et al. [19]), flash and combustion points (UNE 51-023-90), water content (Karl Fisher UNE-EN ISO 12937:2000), cold filter plugging point (CFPP) (UNE-EN 116:1997), saponification value (SV) (UNE-EN 55012), iodine (IV) and acid values (AV) (UNE-EN 14111:2003), and higher heating value (HHV) (higher heating value prediction by saponification and acid values according to Demirbaş [26]).

3. Results and discussion

3.1. *Raw materials and reaction conditions*

3.1.1. *Properties of the raw materials*

Table 1 shows vegetable oils properties and its content of fatty acids. Except *Jatropha Curcas* oil, all oils had small amount of

Table 2 – Basic transesterification conditions and methyl esters content of obtained biodiesel from soybean oil.

Exp.	Transesterification conditions					Methyl esters content
	Catalyst	Methanol:oil molar ratio	Temperature	Agitation rate	Time	
1	1.0 wt.% KOH	9:1	35 °C	700 rpm	120 min	94.6
2	1.0 wt.% KOH	9:1	45 °C	700 rpm	120 min	95.0
3	1.0 wt.% KOH	9:1	55 °C	700 rpm	120 min	97.1
4	**1.0 wt.% KOH**	**9:1**	**65 °C**	**700 rpm**	**120 min**	**97.6**
5	1.0 wt.% KOH	9:1	65 °C	*300 rpm*	120 min	97.3
6	1.0 wt.% KOH	9:1	65 °C	*500 rpm*	120 min	97.5
7	1.0 wt.% KOH	9:1	65 °C	*900 rpm*	120 min	96.9
8	1.0 wt.% KOH	*3:1*	65 °C	700 rpm	120 min	86.1
9	1.0 wt.% KOH	*6:1*	65 °C	700 rpm	120 min	97.1
10	1.0 wt.% KOH	*12:1*	65 °C	700 rpm	120 min	97.9
11	*0.5 wt.% KOH*	9:1	65 °C	700 rpm	120 min	96.1
12	*1.5 wt.% KOH*	9:1	65 °C	700 rpm	120 min	97.5
13	*0.5 wt.% NaOH*	9:1	65 °C	700 rpm	120 min	96.3
14	*1.0 wt.% NaOH*	9:1	65 °C	700 rpm	120 min	97.7
15	*1.5 wt.% NaOH*	9:1	65 °C	700 rpm	120 min	98.5
16	*0.5 wt.%* CH_3OK	9:1	65 °C	700 rpm	120 min	97.2
17	*1.0 wt.%* CH_3OK	9:1	65 °C	700 rpm	120 min	98.3
18	*1.5 wt.%* CH_3OK	9:1	65 °C	700 rpm	120 min	98.5

In Italics: variable which has been studied in each experiment; In bold: the experiment with the highest methyl ester content.

free fatty acids (FFA) and low water content, and, therefore, they showed favorable conditions for a basic transesterification process [27].

First, in this paper, an experimental review of the basic transesterification was conducted in the laboratory reactor, with the aim of optimizing the main process variables: amount and type of basic homogeneous catalyst, agitation rate, methanol molar ratio and reaction temperature. Soybean oil was selected for the optimization process because it presented intermediate characteristics of all oils under study (see Table 1).

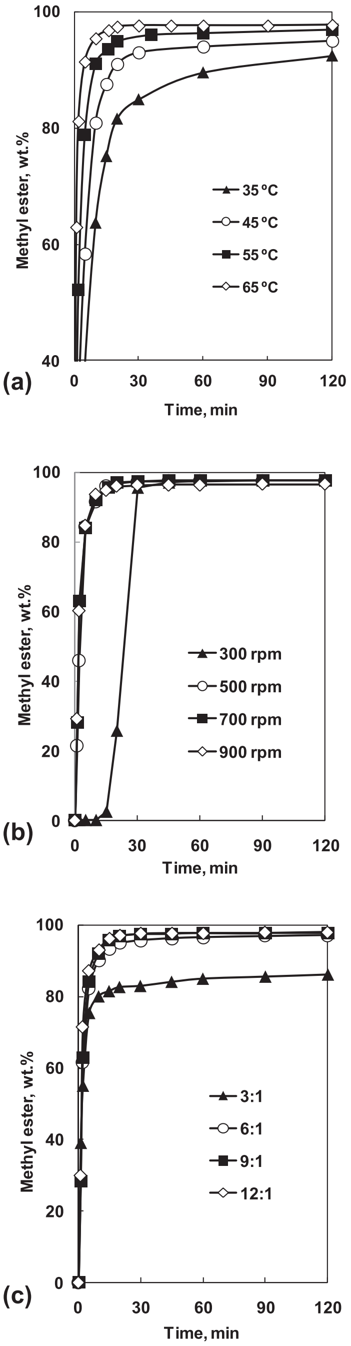

Fig. 1 – Basic transesterification conditions (soybean oil). a) Temperature influence (CH_3OH:oil 9:1; 700 rpm; [KOH], 1.0 wt.%). b) Agitation rate influence (CH_3OH:oil 9:1; 65 °C; [KOH], 1.0 wt.%). c) Methanol molar rate influence (700 rpm; 65 °C; [KOH], 1.0 wt.%).

Because most of properties of biodiesel depend on the used feedstock and, specifically, on its fatty acid content [18], secondly, a study of biodiesel quality in terms of raw material was performed, using the reaction conditions more favorable. Finally, different oil mixtures were tested to achieve better fuel quality, when was possible.

3.1.2. *Basic transesterification optimization. Soybean oil*

To obtain high FAMEs content by basic transesterification of soybean oil, the main variables were tested. These conditions and the methyl esters content of obtained biodiesel are summarized in Table 2.

The influence of reaction temperature was studied at 35, 45, 55 and 65 °C (experiments 1 to 4 in Table 2). As expected, an increase in methyl esters content with increasing of temperature was observed. This is because the effect of temperature on reaction rate is positive, as can be seen in Fig. 1a: as temperature increased, FAMEs formation rate was higher, being 65 °C the optimal temperature.

Mass transference problems could occur during the transesterification process when high methanol/oil molar ratios are used. Alcohol is not soluble in triglycerides for molar ratios over 3:1 [28]. Therefore, if higher relations are used, there is a liquid–liquid process at the beginning of the reaction and its rate could be controlled by the diffusion of the reagents between the phases. The study of agitation rate effect is important for overcoming these problems. As can be seen in Fig. 1b, the mass transference problems were overcome with agitation values greater than 500 rpm. The agitation of 700 rpm was maintained in order to ensure good mixing conditions.

The effect of methanol/oil molar ratio was tested in this work too. As reported in previous research [3], it was found that when methanol molar ratio was increased above the stoichiometric ratio (3:1), FAMEs formation was favored. This is because increasing the amount of methanol the chemical equilibrium was shifted to the biodiesel production. For methanol/oil molar ratios between 6:1 and 12:1, low variability was found, although the molar ratio of 9:1 was the most favorable for the biodiesel production with the proved conditions (see experiments 4 and 8 to 10 in Table 2, and Fig. 1c).

Finally, in order to optimize the catalyst use, different types and amounts of homogeneous basic catalysts were tried. As can be seen in Table 2 (experiments 4 and 11–18), the final results were nearly independent of the type of catalyst, within the used range. Therefore, KOH was selected as basic catalyst because of it is the most commonly employed in the industry. On the other hand, when increasing the amount of every catalyst, methyl esters formation rate increased slightly and amount of 1.0 wt.% was selected as adequate.

To reach a FAMEs content of 97.6 wt.% by basic transesterification of soybean oil, it was necessary a KOH amount of 1.0 wt.% (with respect soybean oil), a methanol/oil ratio of 9:1 and to keep the reaction for 120 min at 65 °C, stirring at 700 rpm. These transesterification conditions were used in subsequent reactions.

Table 3 – Biodiesel quality. Transesterification of pure vegetable oils (Reaction conditions: 1.0 wt.% KOH, 9:1 CH_3OH:oil, 65 °C, 700 rpm, 120 min).

Parameter	Biodiesel fuels							EN 14214
	S	R	SU	HO	CC	BC	JC-p-e.[d]	
Methyl ester content, wt.%	97.6	99.6	99.0	99.5	92.3	88.3	98.1	>96.5
C16:0, wt.%	10.6	4.5	4.5	3.6	7.6	3.0	13.5	
C18:1, wt.%	25.1	66.6	67.6	85.3	25.8	21.4	42.9	
C18:2, wt.%	52.1	17.2	20.9	6.7	41.7	17.2	33.6	
C18:3, wt.%	5.91	7.75	0.03	0.01	3.75	11.41	0.20	
C22:1, wt.%	0.35	<0.01	1.00	<0.01	10.2	33.3	0.18	
Unsaturation degree, UD[a]	143.4	116.8	111.4	99.9	136.5	126.4	112.8	
Density 15 °C, g L^{-1}	885.7	879.6	878.6	876.6	885.7	896.9	881.6	860–900
Kinematic viscosity 40 °C, cSt	4.04	4.42	4.55	4.74	4.66	5.31	4.46	3.50–5.00
Water content, wt.%	0.03	0.02	0.01	0.02	0.01	0.03	0.03	<0.05
Acid value, $mg_{KOH} \cdot g_{oil}^{-1}$	0.24	0.32	0.34	0.32	0.41	0.31	0.28	<0.50
FFA content, %	0.12	0.16	0.17	0.16	0.21	0.16	0.14	
Iodine value, $g_{I2} \cdot 100g_{oil}^{-1}$	120.6	101.5	92.4	84.6	114.8	106.1	96.7	<120
Saponification, $mg_{KOH} \cdot g_{sample}^{-1}$	190.7	185.0	186.0	187.5	189.2	188.1	186.9	
Cetane number[b]	42.6	48.3	51.0	53.2	43.2	46.4	49.2	>51.0
Higher heating value[c], $KJ \cdot g_{sample}^{-1}$	39.80	40.32	40.42	40.47	39.95	40.13	40.32	
Flash point, °C	165	177	161	167	175	177	188	>120
Combustion point, °C	179	193	189	194	197	200	198	
CFPP, °C	−4	−7	1	2	−3	5	1	−20 to 5

[a] Unsaturation degree calculated according to Ref. [19].
[b] Cetane number determined according to Ref. [25].
[c] Higher heating value predicted according to Ref. [26].
[d] JC oil was pre-esterified. Conditions of esterification: 65 °C, 0.5 wt.% of H_2SO_4, 6:1 methanol molar ratio, 45 min.

3.2. *Biodiesel fuels quality. Methyl esters content influence (different vegetable oils)*

Basic transesterification of S, R, SU, HO, CC, BC oils and JC oil pre-esterified (pre-esterification conditions: 65 °C, 6:1 methanol/oil molar ratio, 700 rpm, 0.5 wt.% of H_2SO_4) was carried out under the experimental conditions previously selected.

The main parameters of obtained biodiesel fuels were determined. These parameters and the content of the most important methyl esters are summarized in Table 3, as well as the limits established by the Norm EN 14214. As can be seen, the best results were obtained with R, SU and HO oils (99.6, 99.0 and 99.5 wt.%, respectively), i.e., the oils with higher methyl oleate content (66.6, 67.6 and 85.3 wt.% of methyl oleate, respectively).

3.2.1. *Density*

Density is a key fuel property, which directly affects the engine performance characteristics because many of these characteristics, such as cetane number or heating value, are related to the density [29]. The European EN norm established the density limits in the range of 860–900 g L^{-1}. In this work, densities of all obtained biodiesels were between these values.

Values of biodiesel density will depend on the methyl esters composition and their purity. On the one hand, density will increase with decreasing chain length (number of carbon atoms) and increasing number of double bonds (unsaturation degree, UD). On the other hand, density could be decreased by the presence of low-density contaminants, such as methanol in this case [30].

As can be seen in Table 3, the order of UD of biodiesel fuels is: from S > CC > BC > R > JC > SU > HO. The obtained values of density followed this trend (from 876.6 to 885.7 g L^{-1}), i.e. they increased with increasing of their unsaturation degrees (see Fig. 2). Biodiesel obtained from BC oil was the unique exception (896.9 g L^{-1}). This deviation could be due to its lower purity (88.3 wt%), which results in a considerable amount of non-reacted compounds with a higher density than the FAMEs formed. The deviation cannot be due to the presence of C22:1 (33.3 wt.%) in biodiesel from BC because the density decreases with chain length; and the mentioned deviation is bigger and not lower.

3.2.2. *Kinematic viscosity*

Viscosity is a measurement of the internal friction between molecules or of the resistance to flow of the liquids. In a diesel engine, the liquid fuel is sprayed into compressed air and

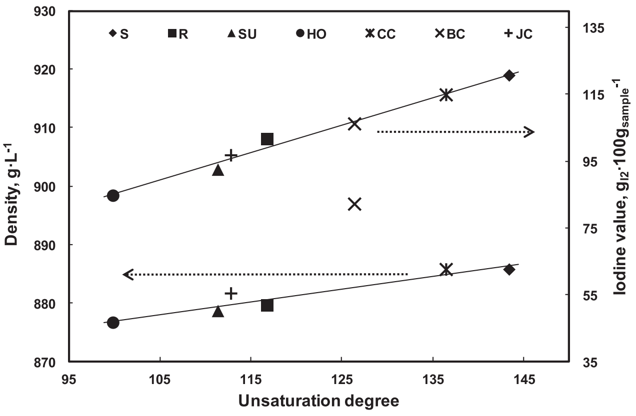

Fig. 2 – Density (left axe) and iodine value (right axe) vs. unsaturation degree.

Table 4 – Kinematic viscosity at 40 °C and cetane number of several pure FAMEs.

	C14:0	C16:0	C16:1	C18:0	C18:1 cis	C18:1[c] trans	C18:2	C18:3	C22:1
Kinematic viscosity at 40 °C[a], cSt	3.30	4.38	3.67	5.85	4.51	5.20	3.65	3.09	7.33
Centane number[b]	66.2	74.3	51.0	75.6	56.5	–	38.2	32.7	76.0

[a] From Ref. [34].
[b] From Ref. [25].
[c] The differentiation between cis and trans methyl oleate was considered only for prediction of viscosity.

atomized into small drops near to the nozzle exit [18]. High values of viscosity give rise to a poor fuel atomization, incomplete combustion, and carbon deposition on the injectors [30–32]. High viscosity also causes more problems in cold weather, because viscosity increases with decreasing temperature [33]. On the other hand, fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear [32]. Kinematic viscosity at 40 °C is limited to 3.5–5.0 cSt in the European EN 14214 norm, and to 1.9–6.0 cSt in the American ASTM D6751 norm.

The kinematic viscosity of fatty compounds is significantly influenced by compound structure as the present data obtained at 40 °C. Influencing factors are chain length, position, number and nature of double bonds, as well as nature of oxygenated moieties. Generally, the hydrocarbons in fossil diesel exhibit lower viscosity in a narrower range than the fatty esters comprising biodiesel and related fatty compounds with dibenzothiophene affecting viscosity of a low-viscosity solvent less than a long chain hydrocarbon and fatty esters. In some cases, the viscosity of the fatty acids comprising a certain feedstock may affect the utility of the resulting esters as biodiesel fuel [32].

Knothe and Steidley predicted the kinematic viscosity of several biodiesels from the kinematic viscosity values of the individual components, with the equation (2) [34]:

$$\upsilon_{\mathrm{mix}} = \sum A_{\mathrm{C}} \cdot \upsilon_{\mathrm{C}} \tag{2}$$

in which υ_{mix} is the kinematic viscosity of the biodiesel sample (mixture of FAMEs), A_{C} is the relative amount (%/100) of the individual methyl ester in the mixture (as determined by GC) and υ_{C} is the kinematic viscosity of every methyl esters at 40 °C (see Table 4).

As can be seen in Fig. 3a, the experimental kinematic viscosity values are very close to predicted kinematic viscosity values. This confirms that the viscosity of biodiesel is directly related to its methyl esters content. The calculated values do not include the unknown components of biodiesel and this lead the differences between the experimental and predicted values.

It is observed that lower viscosity values were obtained for those fuels with less UD (S biodiesel with 4.04 cSt). In fact, if the experimental viscosity versus UD is represented (see Fig. 3b), a linear relationship between both parameters is found for S, R, SU, HO and JC biodiesel, i.e. the group whose contribution to their UD was mainly due to methyl esters C18:1, C18:2 and C18:3 (group with practically the same chain lengths). CC and BC biodiesel, with a higher viscosity, depart from this trend because of its high content of methyl ester C22:1 whose chain length is greater.

3.2.3. *Acid value (AV)*

Acid value is a measurement of the FFA concentration and is influenced by several factors as on the type of raw material used for biodiesel production and its respective degree of refinement. The parameter can also be increased during storage due to hydrolytic cleavage of methyl ester bonds [18]. At last, acidity can be formed during the transesterification process by mineral acids introduced as catalysts or by FFA resulting from acid work-up of soaps, but, due to the analogous motives, it can also be decreased during the production process (by neutralization reaction with mineral basic catalysts or by simultaneous esterification reaction in the process when acid catalysts are used). High fuel acidity has been

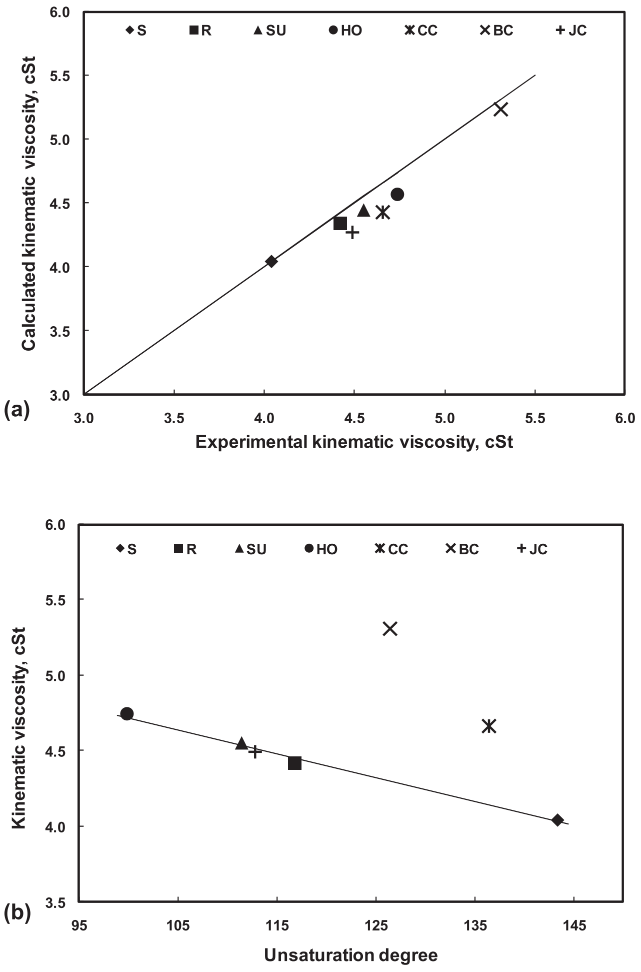

Fig. 3 – a) Calculated vs. experimental kinematic viscosity at 40 °C. b) Experimental kinematic viscosity at 40 °C vs. unsaturation degree.

discussed in the context of corrosion and the formation of deposits within the engine, particularly in fuel injectors, by catalyzing polymerization in hot recycling fuel loops. However, it has been shown that free fatty acids as weak carboxylic acids pose far lower risks than strong mineral acids [35].

The acid values for the analyzed samples are inferior to the maximum value of 0.50 $mg_{KOH} \cdot g_{sample}^{-1}$ that the Norm EN 14214 indicates (between 0.24 and 0.41 $mg_{KOH} \cdot g_{sample}^{-1}$).

3.2.4. *Iodine value (IV)*

Iodine value measures the unsaturation degree of fuel and it is expressed as the percentage in mass of iodine absorbed by mass of sample. Thus, iodine value increases by increasing number of double bonds. This fact is verified in Fig. 2. Therefore, IV depends on the fatty acid distribution in the raw material; and it is independent of the degree of conversion theoretically, because the number of double bonds is not influenced by the transesterification degree. Indeed, comparing values of Tables 1 and 3, it is found that the differences between the feedstock and biodiesel were minimal.

A high iodine value can indicate chemical instability, since the double bonds are quite reactive zones of the molecule [36]. According to this statement, the HO biodiesel (IV = 84.6 $g_{I2} \cdot 100g_{sample}^{-1}$) would be the most stable against the S biodiesel (IV = 120.6 $g_{I2} \cdot 100g_{sample}^{-1}$), the most unstable of the obtained biodiesel whose IV was superior to the limit permitted by Norm EN 14214.

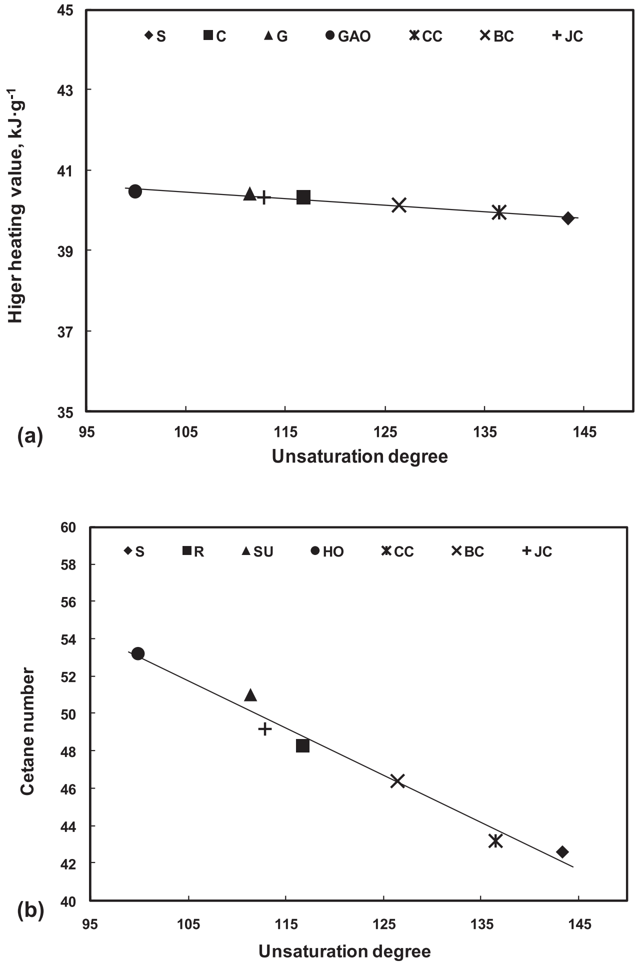

Fig. 4 – a) Higher heating value vs. unsaturation degree 40 °C. b) Cetane number vs. unsaturation degree.

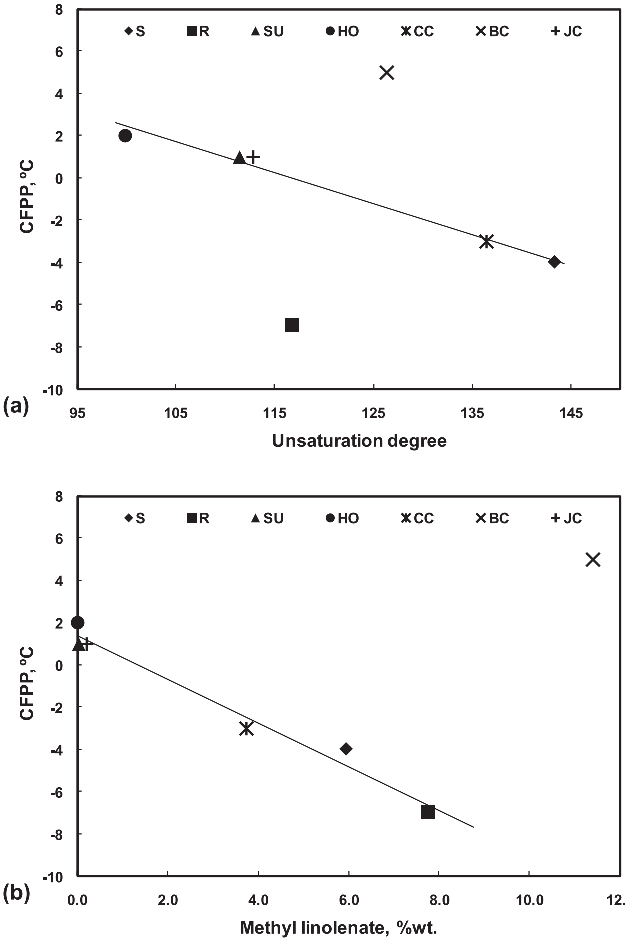

Fig. 5 – a) Cold filter plugging point vs. unsaturation degree. b) Cold filter plugging point vs. methyl linolenate content.

3.2.5. *Saponification value (SV)*

Saponification value (SV) is milligrams of KOH necessary to saponify 1 g of oil sample. It is related to the molecular weight average, so SV of oil decreases with increase of its molecular weight [26]. However, acids from triglycerides are the same as those that form the FAMEs (biodiesel), therefore, molecular weight average does not change significantly and the employed raw material for biodiesel production strongly influences in this parameter [3]. Since in this work the calculated SVs have been used to determine the molecular weights of oils, it not would be valuable to check this trend.

Norm EN 14214 does not set limits for this parameter. The obtained values for the produced biodiesel can be seen in Table 3 (values between 185.0 and 190.7 $mg_{KOH} \cdot g_{sample}^{-1}$).

3.2.6. *Higher heating value (HHV)*

Although biodiesel fuel does not contain aromatics, it contains methyl esters with different levels of saturation. It is known that the heating value increases with increasing chain length and it decreases with increase in the number of double bonds. The increase in heat content results from a high increase in the number of carbons and hydrogens, as well as an increase in the ratio of these elements relative to oxygen. A decrease in heat content is the result of fewer hydrogen atoms (i.e., greater unsaturation) in the molecule [26].

The experimental determination of higher heating value (HHV) and ultimate analysis requires special instrumentation. Therefore, A. Demirbaş [26] developed a mathematical equation to calculate the HHVs of the lignocellulosic fuels from its IV and its SV. On the one hand, SV decreases with increase of the molecular weight and the percentages of carbon and hydrogen increase with decrease in molecular weight. On the other hand, the increase in IV (greater unsaturation) results in a decrease in HHV. With these considerations, equation suggested for calculation of HHVs (kJ g^{-1}) was:

$$\mathrm{HHV} = 49.43 - (0.041 \cdot \mathrm{SV} + 0.015 \cdot \mathrm{IV}) \tag{3}$$

The obtained values are shown in Table 3. HO biodiesel had the highest HHV (40.47 kJ g^{-1}), although the differences of HHVs were minimal. As mentioned previously, IV increased with increasing of unsaturation; therefore as expected, HHV decreased with increasing UD (see the trend shown in Fig. 4a).

3.2.7. *Cetane number (CN)*

Cetane number (CN) is one of the main indicators of the quality of the diesel fuel, because it is related with time of ignition lag of a fuel to the injection in the combustion chamber. High values of CN guarantee a good control of the combustion, increasing therefore the engine efficiency. In addition, fuels with high CN present facility for the cold start, low noise to the slow motion and less polluting gases of exit [36].

Determination of the CN of a fuel by an experimental procedure is a tedious job for the upcoming biodiesel production industry. One of the ways of solving the problem of CN determination is to develop models to predict the CN when some parameters are known. Since the fatty acid composition of base oil predominantly affects the CN of the biodiesel produced from it, models can be developed relating CN to the composition of FAMEs [18].

In this work, CN prediction with the FAMEs composition was realized according to Tong et al. [25], shown in equation (4):

$$\mathrm{CN} = 1.068 \sum (\mathrm{CN_C} \cdot A_\mathrm{C}) - 6.747 \tag{4}$$

in which CN is the cetane number of the biodiesel sample (mixture of FAMEs), A_C is the relative amount (%/100) of the individual methyl ester in the mixture (as determined by GC) and CN_C is the cetane number of every methyl esters (see Table 4).

As can be seen in Table 3 and Fig. 4b, and according to other papers [37], CNs decreased with increasing UD. Thus, only CNs of SU and HO biodiesel (51.0 and 53.2, respectively) were in accordance with the requirements of the Norm EN 14214 (>51.0).

3.2.8. *Cold filter plugging point (CFPP)*

Cold filter plugging point (CFPP) is the temperature at which a fuel causes a plug in the filter due to its crystallization or gelation. Therefore, this parameter is very critical for the

Table 5 – Biodiesel quality. Transesterification of vegetable oil mixtures (Reaction conditions: 1.0 wt.% KOH, 9:1 CH_3OH:oil, 65 °C, 700 rpm, 120 min).

Parameter	Biodiesel fuels													
	50R50S		75R25S		25R75S		50R50HO		75R25HO		25R75HO		33R33S33HO	
	Exp.[d]	Theor.[e]	Exp.[d]	Theor.[e]	Exp.[d]	Theor.[e]	Exp.[d]	Theor.[e]	Exp.[d]	Theor.[e]	Exp.[d]	Theor.[e]	Exp.[d]	Theor.[e]
Methyl ester content, wt.%	99.0	*98.6*	99.3	*99.1*	98.0	*98.1*	99.8	*99.6*	99.7	*99.6*	99.8	*99.5*	99.0	*98.0*
C16:0, wt.%	7.4	*7.5*	5.9	*6.0*	8.8	*9.1*	3.9	*4.0*	4.0	*4.3*	3.6	*3.8*	6.1	*6.2*
C18:1, wt.%	46.5	*45.9*	56.9	*56.2*	35.8	*35.5*	76.7	*76.0*	73.0	*71.3*	81.7	*80.6*	59.6	*58.4*
C18:2, wt.%	35.1	*34.7*	26.0	*25.9*	43.8	*43.4*	11.9	*12.0*	14.6	*14.6*	9.4	*9.3*	25.5	*25.1*
C18:3, wt.%	6.82	*6.88*	7.11	*7.37*	6.22	*6.38*	3.81	*3.94*	5.75	*5.90*	1.89	*1.97*	4.42	*4.54*
Unsaturation degree[a]	131.0	*131.1*	123.5	*123.4*	136.3	*136.8*	109.1	*108.3*	114.3	*112.6*	105.0	*104.1*	119.9	*118.8*
Density 15 °C, g L^{-1}	882.7	*882.7*	880.6	*881.5*	884.7	*884.2*	878.6	*878.1*	879.6	*878.8*	878.6	*877.3*	876.6	*879.7*
Kinematic viscosity 40 °C, cSt	4.26	*4.23*	4.30	*4.33*	4.19	*4.14*	4.61	*4.58*	4.55	*4.50*	4.69	*4.66*	4.39	*4.36*
Water content, wt.%	0.01	—	0.02	—	0.03	—	0.03	—	0.03	—	0.01	—	0.02	—
Acid value, $mg_{KOH} \cdot g_{oil}^{-1}$	0.19	—	0.20	—	0.18	—	0.26	—	0.25	—	0.26	—	0.20	—
FFA content, %	0.10	—	0.10	—	0.09	—	0.13	—	0.13	—	0.13	—	0.10	—
Iodine value, $g_{I2} \cdot 100g_{oil}^{-1}$	113.0	*111.0*	104.6	*106.3*	117.5	*115.8*	92.4	*93.0*	97.1	*97.3*	89.5	*88.8*	101.7	*101.2*
Saponification, $mg_{KOH} \cdot g_{oil}^{-1}$	188.6	*187.8*	187.2	*186.4*	190.1	*189.3*	186.9	*186.3*	186.5	*185.6*	187.4	*186.9*	188.0	*185.8*
Cetane number[b]	46.3	*45.5*	46.6	*46.9*	43.9	*44.0*	50.9	*50.7*	49.8	*49.5*	52.3	*52.0*	48.0	*47.6*
Higher heating value[c], kJ g^{-1}	40.00	*40.06*	40.18	*40.19*	39.87	*39.93*	40.38	*40.36*	40.32	*40.35*	40.40	*40.39*	40.20	*39.78*
Flash point, °C	164	—	164	—	163	—	165	—	169	—	165	—	167	—
Combustion point, °C	189	—	189	—	187	—	189	—	194	—	193	—	187	—
CFPP, °C	−5	−5.5	−6	−6	−4	−4.5	−3	−2.5	−6	−5	−1	−1	−3	−3

In Italics: variable which has been studied in each experiment.

[a] Unsaturation degree calculated according to Ref. [19].

[b] Cetane number determined according to Ref. [25].

[c] Higher heating value predicted according to Ref. [26].

[d] Experimental value.

[e] Theorist value predicted according to equation (5).

diesel engine performance. Norm EN 14214 establishes a limit for moderate climate and other limit for arctic climate, each country can select one of two options (moderate or arctic) for seasonal classes (summer and winter) and modify this specification based on national meteorological data [37].

Bavelaar and Beynen found that the slip point, the temperature which starts to flow into a capillary tube, had a negative correlation with the ratio of the unsaturated to saturated fatty acids [38] and, in this sense, Park et al. reported that CFPP values increased with increasing saturation of oils [39].

In Fig. 5a this trend is tested but it is found that R and BC biodiesel away than expected. When studying CFPP values as a function of methyl linolenate content (see Fig. 5b) was found that as increasing amount of C18:3, CFPP decreased, including R biodiesel (CFPP = −7 °C). This shows the great influence of this ester on CFPP values. However, BC biodiesel was also an exception in this sense. High value of CFPP of BC biodiesel (5 °C) could be due to its lower purity, and thus its higher content of other components such as tri-, di- and monoglycerides, in addition to their higher content of esters with longer chain (C22:1).

3.2.9. *Flash and combustion points*

Flash point measures the tendency of a sample to form inflammable mixtures with air, under controlled conditions of laboratory. Combustion point is the temperature to which a flame brings about the continued inflammation of a fuel. Combustion point is usually greater to flash point and both points are related to the security in the storage and fuel handling. High values of both points diminish the fire risk and make more insurance and stable the storage. In addition, it is known that very small quantities of residual alcohol present in biodiesel provoke a significant decrease in the flash point. Boog et al. found that there is a direct correlation between the flash point and the residual alcohol content in the prepared biodiesel [40]. According to this paper, biodiesel with the minimum flash point demanded by the Norm EN 14214, 120 °C, cannot have an alcohol concentration higher that 0.1% wt.

The obtained results of flash and combustion points were much higher that established by European Norm (flash point from 161 to 188 °C; combustion point from 179 to 200 °C), and therefore it can be assumed that obtained biofuels had not residual alcohol content.

3.2.10. *Water content*

Water presence in biodiesel can cause oxide formation and corrosion. In addition, it aid to the microbial growth that can happen in the interface between biodiesel and free water. The Norm EN 14214 allows a water content of 500 mg kg^{-1}, that is to say, a 0.05 wt.%, for not to exceed the solubility of the water in biodiesel (~1500 mg kg^{-1}) and thus to avoid that the water remains suspended [36]. As it is observed in Table 3, the biodiesel obtained in this work did not exceed the maximum water content permitted by EN 14214 (obtained values between 0.01 and 0.03 wt.%).

3.3. *Improving of biodiesel quality. Mixtures of oils*

The discussed results reveal that if the raw material is not adequate, it might produce a biodiesel which not meet the requirements of Norm EN 14214. A possible solution is to mix the raw materials. In this work, several mixtures of oils at different proportions by weight were also prepared for biodiesel production: rapeseed and soybean oils (50R50S; 75R25S; 25R75S), rapeseed and high oleic sunflower oils (50R50HO; 75R25HO; 25R75HO), and rapeseed, soybean and high oleic sunflower oils (33R33S33HO).

The properties of obtained biofuels are shown in Table 5. It finds that, with the same process conditions and knowing properties of biodiesel from pure oils, and assuming that the mixture behaves in ideal form with respect to the properties that dependent on the content of methyl esters, these properties of biodiesel from oils mixture can be predicted according to follow equation:

$$P_{BD_{MIX}} = \sum A_{OIL} \cdot P_{BD_{OIL}} \tag{5}$$

in which P_{BDMIX} is the property of biodiesel from oils mixture, A_{OIL} is the relative amount (%/100) of oil in initial mixture and P_{BDOIL} is the same property of every biodiesel from the pure oil (shown in Table 3).

As expected, Table 5 (concretely in columns with italic font) shows that equation (5) predicted the methyl ester content of biodiesel from mixtures successfully, therefore this equation was also applicable to predict those properties dependent the methyl esters distribution: density, kinematic viscosity, iodine value, cetane number, higher heating value and cold filter plugging point. All predicted values were very close to experimental values.

On the other hand, the equation (5) is not applicable to predict water content, acid value or flash and combustion points because they were more influenced by transesterification and purification processes than by raw material.

Finally, comparing values shown in Table 3 and values shown in Table 5, it is checked that, for example, the CFPP, density and kinematic viscosity of HO biodiesel can be improved using HO and R oils mixtures in the biodiesel production, i.e., it is proved that using mixtures of determined oils, it is possible to modify the properties of biodiesel.

4. Conclusions

In summary, as expected, properties such as density, kinematic viscosity, iodine value, cetane number, higher heating value and cold filter plugging point depend largely on the unsaturation degree of biodiesel, i.e., on its methyl esters distribution, or the fatty acids distribution of raw materials. Thus, on the one hand, HO biodiesel, with the lowest UD (99.9), had the highest values of CN, HHV and viscosity (excepting viscosity of BC biodiesel because of motives exposed previously); and the lowest values of density and IV. On the other hand, S biodiesel (UD = 143.4) showed the lowest values of CN, HHV and viscosity; and the highest values of IV and density (excepting density of BC biodiesel because of motives exposed previously). In respect to CFPP, R biodiesel had the lowest value due to its high methyl linolenate content. Other properties such as water content, acid value or flash and combustion points were more influenced by transesterification and purification processes than by raw material.

In order to improve the quality of biodiesel, it is possible to use oils mixtures in biodiesel production. In addition, with the same process conditions and knowing properties of biodiesel from pure oils; for biodiesel from oils mixtures, its methyl esters content, and therefore properties dependent this content can be predicted from a simple mathematical equation.

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REFERENCES

[1] Demirbas A. Biodegradability of biodiesel and petrodiesel fuels. Energy Sour A Recov Uti Env Eff 2009;31:169–74.

[2] Coronado CR, de Carvalho Jr JA, Yoshioka JT, Silveira JL. Determination of ecological efficiency in internal combustion engines: the use of biodiesel. Appl Therm Eng 2009;29:1887–92.

[3] Encinar JM, González JF, Rodríguez-Reinares A. Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel. Ind Eng Chem Res 2005;44:5491–9.

[4] Petrou EC, Pappis CP. Biofuels: a survey on pros and cons. Energy Fuels 2009;23:1055–66.

[5] Basha SA, Gopal KR, Jebaraj S. A review on biodiesel production, combustion, emissions and performance. Renew Sustain Energy Rev 2009;13:1628–34.

[6] Enweremadu CC, Mbarawa MM. Technical aspects of production and analysis of biodiesel from used cooking oil—a review. Renew Sustain Energy Rev 2009;13:2205–24.

[7] Pinzi S, Garcia IL, Lopez-Gimenez FJ, Luque de Castro MD, Dorado G, Dorado MP. The ideal vegetable oil-based biodiesel composition: a review of social, economical and technical implications. Energy Fuels 2009;23:2325–41.

[8] Srinivasan S. The food v. fuel debate: a nuanced view of incentive structures. Renew Energy 2009;34:950–4.

[9] Encinar JM, González JF, Rodríguez JJ, Tejedor A. Biodiesel fuels from vegetable oils: transesterification of cynara cardunculus L. oils with ethanol. Energy Fuels 2002;16:443–50.

[10] Gominho J, Lourenço A, Palma P, Lourenço ME, Curt MD, Fernández J, et al. Large scale cultivation of Cynara cardunculus L. for biomass production—a case study. Ind Crops Prod 2011;33:1–6.

[11] Raccuia SA, Piscioneri I, Sharma N, Melilli MG. Genetic variability in Cynara cardunculus L. domestic and wild types for grain oil production and fatty acids composition. Biomass Bioenergy 2011;35:3167–73.

[12] Koh MY, Mohd Ghazi TI. A review of biodiesel production from Jatropha curcas L. oil. Renew Sustain Energy Rev 2011;15:2240–51.

[13] Cardone M, Mazzoncini M, Menini S, Rocco V, Senatore A, Seggiani M, et al. Brassica carinata as an alternative oil crop for the production of biodiesel in Italy: agronomic evaluation, fuel production by transesterification and characterization. Biomass Bioenergy 2003;25:623–36.

[14] Bouaid A, Martinez M, Aracil J. Production of biodiesel from bioethanol and Brassica carinata oil: oxidation stability study. Bioresour Technol 2009;100:2234–9.

[15] Mukta N, Sreevalli Y. Propagation techniques, evaluation and improvement of the biodiesel plant, Pongamia pinnata (L.) Pierre—a review. Ind Crops Prod 2010;31:1–12.

[16] Araujo VKWS, Hamacher S, Scavarda LF. Economic assessment of biodiesel production from waste frying oils. Bioresour Technol 2010;101:4415–22.

[17] Charoenchaitrakool M, Thienmethangkoon J. Statistical optimization for biodiesel production from waste frying oil through two-step catalyzed process. Fuel Process Technol 2011;92:112–8.

[18] Refaat AA. Correlation between the chemical structure of biodiesel and its physical properties. Int J Environ Sci Tech 2009;6:677–94.

[19] Ramos MJ, Fernández CM, Casas A, Rodríguez L, Pérez Á. Influence of fatty acid composition of raw materials on biodiesel properties. Bioresour Technol 2009;100:261–8.

[20] Jena PC, Raheman H, Prasanna Kumar GV, Machavaram R. Biodiesel production from mixture of mahua and simarouba oils with high free fatty acids. Biomass Bioenergy 2010;34:1108–16.

[21] García M, Gonzalo A, Sánchez JL, Arauzo J, Peña JÁ. Prediction of normalized biodiesel properties by simulation of multiple feedstock blends. Bioresour Technol 2010;101:4431–9.

[22] Encinar JM, González JF, Pardal A, Martínez G. Rape oil transesterification over heterogeneous catalysts. Fuel Process Technol 2010;91:1530–6.

[23] Encinar JM, Sánchez N, Martínez G, García L. Study of biodiesel production from animal fats with high free fatty acid content. Bioresour Technol 2011;102:10907–14.

[24] Prankl H. High biodiesel quality required by European Standards. Eur J Lipid Sci Technol 2002;104:371–5.

[25] Tong D, Hu C, Jiang K, Li Y. Cetane number prediction of biodiesel from the composition of the fatty acid methyl esters. J Am Oil Chem Soc 2011;88:415–23.

[26] Demirbaş A. Fuel properties and calculation of higher heating values of vegetable oils. Fuel 1998;77:1117–20.

[27] Zhang Y, Dubé MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Bioresour Technol 2003;89:1–16.

[28] Vicente G, Martinez M, Aracil J. Biodiésel: una alternativa real al gasóleo mineral. Ing Quim 2001;377:135–45.

[29] Tat M, Van Gerpen J. The specific gravity of biodiesel and its blends with diesel fuel. J Am Oil Chem Soc 2000;77:115–9.

[30] Alptekin E, Canakci M. Determination of the density and the viscosities of biodiesel-diesel fuel blends. Renew En 2008;33:2623–30.

[31] Knothe G, Steidley KR. Kinematic viscosity of biodiesel components (fatty acid alkyl esters) and related compounds at low temperatures. Fuel 2007;86:2560–7.

[32] Knothe G, Steidley KR. Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. Fuel 2005;84:1059–65.

[33] Joshi RM, Pegg MJ. Flow properties of biodiesel fuel blends at low temperatures. Fuel 2007;86:143–51.

[34] Knothe G, Steidley KR. Kinematic viscosity of fatty acid methyl esters: prediction, calculated viscosity contribution of esters with unavailable data, and carbon–oxygen equivalents. Fuel 2011;90:3217–24.

[35] Cvengroš J. Acidity and corrosiveness of methyl esters of vegetable oils. Eur J Lipid Sci Technol 1998;100:41–4.

[36] Prakash CB. A critical review of biodiesel as a transportation fuel in Canada. A Technical Report GCSI – Global Change Strategies International, Canada; 1998.
[37] Knothe G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process Technol 2005;86:1059–70.
[38] Bavelaar FJ, Beynen AC. Relationships between dietary fatty acid composition and either melting point or fatty acid profile of adipose tissue in broilers. Meat Sci 2003;64:133–40.
[39] Park J-Y, Kim D-K, Lee J-P, Park S-C, Kim Y-J, Lee J-S. Blending effects of biodiesels on oxidation stability and low temperature flow properties. Bioresour Technol 2008;99:1196–203.
[40] Boog JHF, Silveira ELC, de Caland LB, Tubino M. Determining the residual alcohol in biodiesel through its flash point. Fuel 2011;90:905–7.