Analysis of used frying fats for the production of biodiesel

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RESUMEN

Análisis de aceites y grasas de fritura para producción de biodiesel

Los aceites y grasas de fritura, que se caracterizan por tener una calidad muy variable, se utilizan como material prima para la producción de biodiesel. El objetivo de este estudio es definir la utilidad de los métodos analíticos desarrollados para los aceites y grasas de fritura para caracterizar el biodiesel obtenido. Veinticuatro aceites de fritura procedentes del sector de restauración y de fritura doméstica fueron analizados antes y después de su transesterificación a ésteres metílicos de ácidos grasos. A partir de un análisis detallado mediante cromatografías de adsorción y exclusión, se deduce la importancia cuantitativa de los compuestos de polimerización tanto en el análisis directo de los aceites como en el análisis de los ésteres metílicos. Se encontró una excelente correlación lineal entre los compuestos polares y los ésteres metílicos polares (R = 0.9768). Se definen las interferencias de los compuestos formados durante la fritura en el análisis estándar para conocer la calidad del biodiesel y se propone la determinación de ésteres metílicos no polares como una buena alternativa a la determinación cromatográfica estándar.

PALABRAS – CLAVE: *Aceites y grasas de fritura – Análisis – Biodiesel – Compuestos polares – Esteres metílicos de ácidos grasos polares.*

SUMMARY

Analysis of used frying fats for biodiesel production

Used frying fats and oils with highly variable and uncontrolled quality are used for the production of biodiesel . The objective of this study was to define the analytical methods useful to obtaining information on the quality of the used frying oils as raw material for biodiesels as well as for the characterization of the biodiesels obtained from them. Twenty-four used frying oils from restaurants and domestic fryers were analyzed before and after transesterification to fatty acid methyl esters (FAME). From a detailed analysis of the samples by means of a combination of adsorption and size exclusion chromatography, the quantitative importance of polymeric compounds was deduced both from the direct analysis of the oils and from their FAME. Excellent linear correlation between polar compounds and polar FAME (R = 0.9768) was found. The possibilities of interferences from polar fatty acid in the standard method to determine the ester content are defined. Finally, determination of non-polar FAME by silica column is proposed as a good alternative to the gas chromatography method.

KEY-WORDS: *Analysis – Biodiesel - Polar compounds – Polar fatty acid methyl esters – Used frying oils.*

1. INTRODUCTION

The base-catalyzed transesterification method is normally applied for biodiesel production. However, biodiesel produced from crude or refined oils is usually more expensive than petroleum-based diesel fuel. The recent concerns over sustainability, environmental issues, and raw material costs have made the use of used frying oils very attractive to the industry. In this respect, there have been a significant number of studies over the last decade with the aim of establishing the optimum conditions for biodiesel production using frying oils as raw material (Costa Neto *et al.*, 2000; González Gómez *et al.*, 2002; Leung, 2001; Al-Widyan *et al.*, 2002; Supple *et al.*, 2002; Tashtoush et al, 2004; Tomasevic and Siler-Marinkovic, 2003; Zhang *et al.*, 2003 a, b; Felizardo *et al.*, 2006; Leung and Guo, 2006) or evaluating their performance as fuels (Mittelbach and Tritthart,1988; Al-Widyan and Al-Shyoukh, 2002; Zaher, 2003; Dorado *et al.*,2003; Ulusoy el al., 2004).

However, used frying oils from restaurants and food industries have a wide variety of qualities. During the frying process, the oil or fat is exposed to high temperatures in the presence of air and moisture. Under these conditions, they may undergo important changes due to hydrolytic, oxidative and thermal reactions resulting in the loss of quality of the frying oil and of the fried food. Changes in the main fat constituents are known, although it is not easy to foresee the rate of oil degradation due to the high number of variables involved in the frying process. Some of them are linked to the process itself, such as temperature, length of heating, continuous or discontinuous heating, turnover period, etc.; others to the food subjected to frying, i.e. lipid composition, main and minor constituents, etc.; or else to the fat or oil used e.g., unsaturation degree, initial quality and additives (Varela, 1985; Rodrigues Machado *et al.*, 2007).

The new products formed during frying are polymers, dimers, oxidized triglycerides, as well as diglycerides and fatty acids (Dobarganes and Márquez-Ruiz, 2006). All these groups possess higher polarity than that corresponding to the initial triglycerides and can be easily quantified by means of adsorption chromatography (IUPAC, 1992). Thus, polar compound determination gives a good measurement of the total degradation of frying oils

and, for this reason, it is not only the most accepted method in the evaluation of frying fats but also the limitation of the alteration of frying fats for human consumption in polar compound levels around 25 % has been included in many official regulations (Firestone, 1996). Even more, analyses of used frying oils sampled by the Food Inspection Services in different countries have clearly demonstrated that the stated 25% polar compounds is overpassed in a significant number of used frying oils (Dobarganes and Márquez Ruiz, 1995a, 1995b, 1998).

Thus, used frying oils can be highly heterogeneous as compared to crude or refined oils. In general, it is found that crude oils have more than 95% of triglycerides + partial glycerides which would give more than 98% of fatty acid methyl esters (FAME) supposing that total tranesterification takes place. However, in the case of used frying oils, non-altered FAME depends on the variable quality of the used frying oil (Dobarganes et al., 1984; Márquez Ruiz et al., 1995). At present, the quantification of the main groups of degradation compounds in used frying oils (Dobarganes et al, 1988, 2000) as well as in the FAME obtained after oil transesterification (Dobarganes et al, 1984; Márquez Ruiz et al., 1990) is not a difficult task and takes advantage of the two main properties differentiating the new compounds formed during frying from the initial TG, i.e. polarity and molecular weight (MW).

On the other hand, studies are necessary to clarify the new compounds present in used frying fats and oils as many of the new compounds formed during frying might interfere in the standard gas chromatographic determinations for evaluating the quality of biodiesel (European Standard, 2003a; 2003b).

The objective of this study was to define the analytical methods useful to obtaining information on the compounds present in used frying oils and to characterize the biodiesels obtained from them.

2. EXPERIMENTAL PART

2.1. Samples

Twenty-four used frying fats and oils were selected from those collected in restaurants and domestic fryers. Most of the samples had degradation levels close to that established for discarding used frying fats and oils for human consumption (25% polar compounds)

2.2. Analytical techniques

Quantification of polar compounds and their distribution in oxidation, polymerization and hydrolytic compounds. Non-polar and polar fractions were separated from 1g of oil sample by silica column chromatography (20 g silica-H_2O, 95:5 w/w). Non-polar fraction containing unaltered TG was eluted with 150 mL of n-hexane/diethyl ether (90:10, v/v). A second fraction, comprized of total polar compounds, was eluted with 150 mL of diethyl ether. Efficiency of the separation by adsorption chromatography was checked by TLC using hexane/diethyl ether/acetic acid (80:20:1, v/v/v) for development of plates and exposure to iodine vapor to reveal the spots. After evaporation of solvents, both fractions were weighed and dissolved in diisopropyl ether (25 mg/mL) for analysis by high-performance size exclusion chromatography (HPSEC), using a Rheodyne 7725i injector with 10-mL sample loop, a Waters 510 pump (Waters, Milford, MA, USA), a HP 1037 A refractive index detector and a HP 3392 A integrator (Hewlett-Packard, Avondale, PA, USA). The separation was performed on two 100 and 500Å Ultrastyragel columns (25 cm x 0.77 cm i.d.) packed with porous, highly cross linked styrene-divinylbenzene copolymers (film thickness: 10 mm) (Hewlett-Packard, Avondale, PA, USA) connected in series, with tetrahydrofuran (1 mL/min) as the mobile phase (Dobarganes et al., 2000). The groups of compounds separated were oligomeric triglycerides (OTG), dimeric triglycerides (DTG), oxidized monomeric TG (oxMTG), diglycerides (DG) and Fatty acids (FA) .

Quantification of polar fatty acid methyl esters and their distribution in oligomeric, dimeric and oxidized monomeric FAME. FAME were obtained by transesterification of oil samples with sodium methoxide and hydrochloric acid-methanol and subsequent recovery of methyl esters (Dobarganes et al., 1984). Methyl esters were separated by silica column chromatography, using hexane/diethyl ether (95:5) to elute a non-polar fraction and diethyl ether and methanol to obtain the polar fraction. Analysis of the polar fraction was performed by HPSEC, using the chromatographic conditions described above. The groups of compounds separated were oligomeric FAME (OFA), dimeric FAME (DFA) and oxidized monomeric FAME (OxMFA). The methodology was described in detail, including calibration and reproducibility data, in an earlier publication (Márquez-Ruiz et al., 1990).

Determination of fatty acid methyl esters was performed following the IUPAC Standard Method (IUPAC, 1992).

3. RESULTS AND DISCUSSION

Table 1 shows the evaluation of polar compounds and their distribution in the used frying oils selected. It is interesting to note that samples with the same percentage of total polar compounds showed different patterns of compound distribution. Thus, samples 8, 17, 21 and 22 had high contents of DG formed by hydrolysis while for the rest of the samples the compounds formed by oxidation and high temperature stood out. Such differences between samples are not unusual , considering that previous treatment is unknown and they may have been subject to very different procedures , especially in terms of frying temperature, frying

Table 1
Quantitative determination of total polar compounds and their distribution in used frying oils

Sample	Polar Compounds and distribution (%)					
	Total	OTG	DTG	OxMTG	DG	FA
1	14,5	1,1	5,4	5,6	2,1	0,4
2	17,4	2,1	7,7	5,9	1,2	0,5
3	21,1	3,7	8,8	6,1	1,9	0,6
4	22,8	3,3	7,3	8,9	3,1	0,3
5	23,0	3,3	8,2	9,1	1,9	0,4
6	23,1	4,0	9,2	6,8	2,5	0,6
7	25,5	4,7	9,0	8,6	2,6	0,7
8	25,5	2,7	7,1	8,6	6,9	0,1
9	25,7	6,3	9,4	5,9	3,5	0,6
10	26,4	5,5	8,9	6,4	5,1	0,5
11	26,6	4,9	11,3	8,7	1,2	0,4
12	27,5	6,2	9,8	7,7	3,4	0,4
13	27,6	6,5	10,9	7,2	2,3	0,6
14	27,6	3,7	7,3	9,4	6,2	1,1
15	28,9	5,0	12,5	9,8	1,2	0,4
16	30,8	5,9	9,8	11,5	3,2	0,4
17	33,1	6,5	7,2	5,4	12,3	1,7
18	35,2	8,6	14,0	10,8	1,4	0,4
19	37,3	10,6	14,3	9,0	2,8	0,7
20	39,2	10,5	13,6	9,8	4,5	0,9
21	39,7	7,8	9,8	13,3	7,6	1,2
22	43,5	12,1	13,9	10,0	6,9	0,7
23	47,1	12,3	13,3	15,2	5,7	0,7
24	49,7	21,1	13,5	10,9	3,4	0,8

Abreviations: OTG, Olimeric triglycerides; DTG, dimeric triglycerides; OxMTG, oxidized monomeric triglycerides; Dg, diglycerides; and FA, fatty acids.

periods and total period of use. However, polymeric TG, i.e. oligomeric + dimeric TG were the major constituents in all the samples as previously reported (Marmesat *et al.*, 2007).

Table 2 summarizes the content of polar FAME and their distribution in oligomeric, dimeric and oxidized monomeric TG after tranesterification of the samples. In the second column the percentage of non-polar FAME has also been included. Figure 1 shows typical chromatograms obtained by exclusion chromatography of the two fractions previously obtained by silica column. As can be observed, non-

polar fraction is a single peak constituted by non-polar FAME; while in the polar fraction three main groups of compounds were separated: oligomeric TG (MW > 900), dimeric TG (MW around 600) and oxidized monomeric TG (MW around 300).

As compared to the polar compounds in Table 1, the percentages of polar FAME were much lower as they only include the modified fatty acyl groups present in the TG molecules. Non-polar FAME include not only non-altered fatty acids from all the TG molecules but also those present in DG and fatty acids. Consequently, polar FAME is a direct measurement of thermoxidative degradation affecting unsaturated fatty acids. The results in Table 2 show that polymeric fatty acids (oligomeric + dimeric FAME) were the major compounds. Regression between polar compounds and polar FAME are presented in Figure 2 where the equation of the line as well as the high correlation coefficient found have been included. From the equation it can be deduced that a level of around 10% polar FAME is expected from samples around the level of used frying oil rejection (25% polar compounds).

It is important to note that analysis of polar FAME can be directly applied to biodiesels and that the results obtained would be parallel to those given in table 2 for used frying oils of a similar level of degradation. Thus, after biodiesel production polymeric FAME, i.e. oligomeric + dimeric FAME, as well as oxidized monomeric FAME are expected. Determination of non-polar FAME by adsorption chromatography is an interesting method due to its accuracy in obtaining information on the quality of
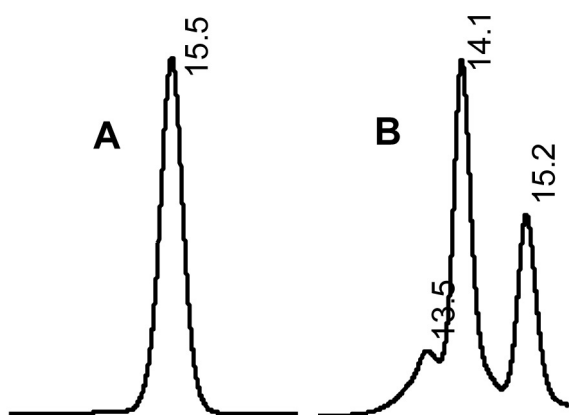

Figure 1
Partial high-performance size-exclusion chromatograms of non-polar fatty acid methyl esters (A) and polar fatty acid methyl esters (B). Retention times : 13.5 min, Oligomeric FAME; 14.1 min, Dimeric FAME; 15.2 min, oxidized monomeric FAME; 15.5 min, non-polar FAME.

Table 2
Quantitative determination of total polar fatty acid methyl esters and their distribution in used frying oils

Sample	Non-polar FAME (%)	Polar FAME and their distribution (%)			
		Total	Oligomeric FAME	Dimeric FAME	Oxidized monomeric FAME
1	94,5	5,5	0,7	2,0	2,9
2	93,2	6,8	0,9	3,3	2,6
3	91,4	8,6	0,8	5,0	2,8
4	91,3	8,7	1,2	4,0	3,6
5	91,0	9,0	0,6	5,1	3,3
6	90,9	9,1	0,8	5,1	3,3
7	89,6	10,4	1,1	5,9	3,4
8	90,6	9,4	0,5	5,2	3,7
9	89,5	10,5	1,3	5,7	3,5
10	89,2	10,8	0,7	6,7	3,4
11	87,9	12,1	1,2	6,2	4,7
12	89,3	10,7	1,1	6,2	3,4
13	88,7	11,3	1,1	6,5	3,7
14	90,3	9,7	0,5	5,5	3,8
15	88,4	11,6	1,1	7,4	3,1
16	86,3	13,7	2,7	6,2	4,7
17	85,1	14,9	3,5	7,4	4,0
18	82,7	17,3	3,8	8,6	4,9
19	84,4	15,6	2,4	8,8	4,4
20	84,9	15,1	2,9	8,4	3,8
21	83,7	16,3	2,5	9,5	4,3
22	83,7	16,3	4,1	8,3	3,9
23	79,0	21,0	5,3	9,8	5,9
24	77,0	23,0	6,1	10,3	6,6

the biodiesel as an alternative to the standard method by gas chromatography.

On the other hand, as stated for animal fats and lauric oils (Schober *et al.*, 2006), the standard method EN14103 by GC (European Standard, 2003b) may give misleading results depending on the level of polar FAME, as many compounds formed may elute between fatty acids ranging from C 12:0 and C 24:1. In this respect, even if polymeric FAME are the major compounds and they are non-

eluted materials in FAME analysis by GC, oxidized fatty acid monomers are also important from a quantitative point of view and they elute in the GC analysis.

Separation and identification of the main structures in FAME from used frying fats indicate that compounds with molecular weight lower than or similar to that of the original fatty acids are present. Among the first group, the short-chain FAME, the short-chain n-oxo FAME and diacid

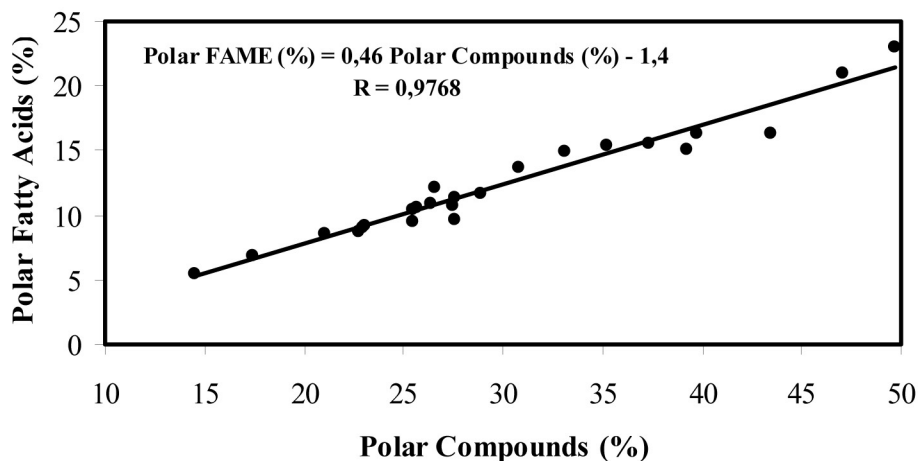Polar FAME (%) = 0,46 Polar Compounds (%) - 1,4
R = 0,9768

Figure 2
Linear regression between polar compounds and polar fatty acid methyl esters.

FAME, originally TG-bound aldehydes and acids resulting from hydroperoxide breakdown, are the most representative compounds (Márquez Ruiz and Dobarganes, 1996; Velasco *et al.*, 2005) Concerning oxidized compounds of molecular weight similar to that of the starting fatty acids, the main groups present corresponded to epoxyacids, ketoacids and hydroxyacids (Velasco *et al.*, 2004).

Figure 3 shows a chromatogram of used sunflower frying oil. The zone corresponding to retention times including C22:0 and C24:0 has been widened to observe the differences between FAME obtained from a refined sunflower oil and from the same oil used in frying until the rejection limit (25%). The oxidized fatty acids formed and eluting would be included in the ester content given by the standard method and may suppose an overestimation between 1 and 2%.

Interferences from monomeric and polymeric FAME can be also found in the application of the standard method (European Standard, 2003b) where a high temperature is applied for the elution of TG and partial glycerides. Studies on this point are being carried out and the results will be reported shortly .

4. CONCLUSIONS

a) The determination of polar fatty acids in biodiesels allows for the exact determination of non-polar esters and is an interesting alternative to the GC standard method due to its accuracy and to the fact that no instrumental techniques are required.

b) From the percentage of polar compounds in used frying fats and oils, the percentage of non-polar and polar methyl esters after the production of biodiesel can be roughly deduced given the excellent correlation between both determinations.

c) Compounds from polar FAME could be present in the chromatograms obtained from present techniques for the quality evaluation of biodiesel when used frying fats and oils are used for biodiesel production.

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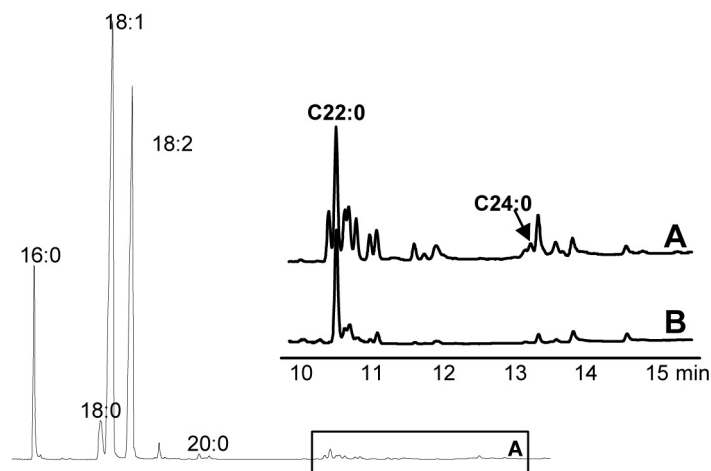

Figure 3
Chromatogram corresponding to the fatty acid methyl esters of used frying sunflower oil
and significant part showing the differences between (A) used frying sunflower oil and (B) initial sunflower oil.

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