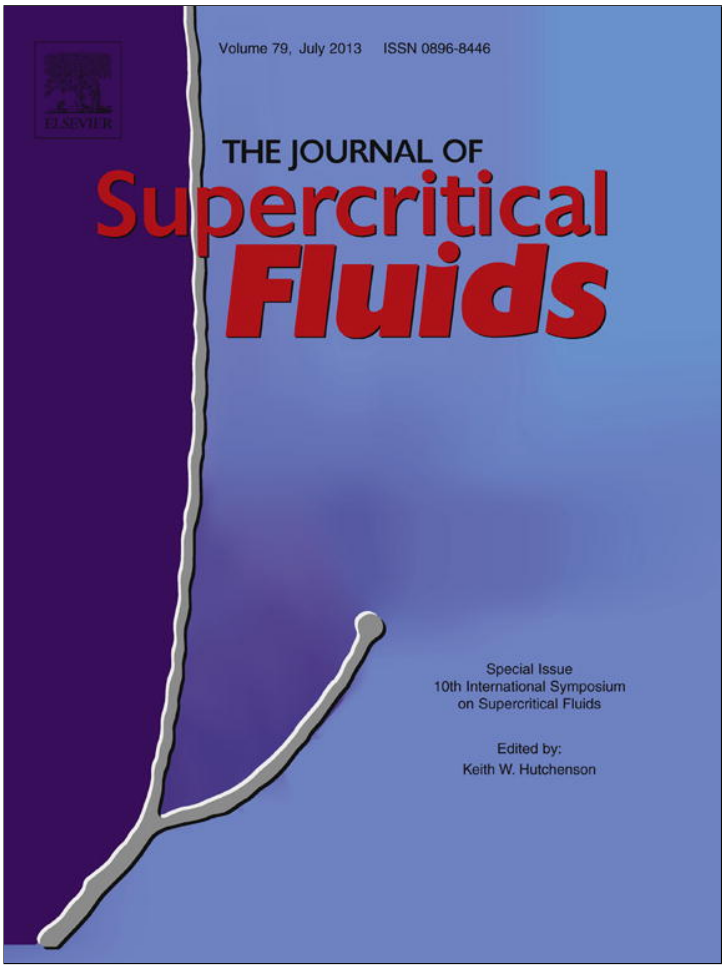

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Fatty acids recovery from vegetable oil wet sludge by supercritical alcoholysis

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ABSTRACT

In the last decade the production of soybean and sunflower oil has greatly increased worldwide. Together with it, the market of the oil refining by-products, phospholipids sludge (wet gum) and distillates of the deodorizer (DDEO) is rapidly changing. In this work, we performed the direct alcoholysis of the phospholipids and oil enclosed in the wet gum using supercritical ethanol. A statistical design of experiments was carried out to determine the effect of temperature (280–320 °C), ethanol concentration (50–80 wt%), reaction time (20–50 min) and water content (51–2.4 wt%). In all the cases a complete conversion of the lipids was observed. After removal of volatile compounds, the reaction product contained a hexane insoluble solid substrate (around 25%) and an oily phase with more than 50 wt% of fatty esters.

1. Introduction

Methyl and ethyl esters production has nowadays a high industrial interest because of its direct use as biodiesel. In general, this biofuel is obtained by the transesterification of refined vegetable oils (palm, rapeseed, soybean, etc.) with methanol, in the presence of an alkaline catalyst to produce methyl esters and glycerine [1].

Different works in the literature point out that the cost of raw material is the major factor affecting the economical viability of biodiesel production [2–4]. In this sense, raw vegetable oils, animal fats and waste cooking oils have been proposed as an alternative triglyceride source for the process [5]. However, biodiesel commercial production is currently carried out with alkaline catalysts, which only achieves high yields when using as the raw-material refined oil without free fatty acids, phospholipids or water [1]. On the other hand, the extraordinary increase of worldwide production of vegetable oil impacted, not only in the oil market, but also in the oil refining by-products (phospholipids sludge and distillates of the deodorizer) [6]. Even though these residues contain high value added products, their cost are decreasing, and they are sometimes becoming a waste, with the related disposal problems [7]. Particularly, soy oil has a high concentration of phospholipids, thus an important volume of sludge (also called gums) is being produced. Nowadays, a small fraction of gums is used to recover high value added products, like lecithin, while most of it is mainly used as ingredient for animal feed. However, soy gums are of low quality for this purpose due to their low nutritive value (high water content) compared to gums derived from other vegetable oils. Furthermore, sludge processing to recover oil or phospholipids is complex. Because of its high viscosity and poor flow properties (sticky behavior), its processing needs large volumes of solvent, and consequently, it is expensive.

In this work, we performed the direct alcoholysis of phospholipids and vegetable oil (triglycerides) occluded in the wet gum using supercritical ethanol to produce fatty acids ethyl esters (FAEE). The use of soybean and sunflower oil gums (SOGs) as low cost feedstocks can be exploited for biodiesel production. Sunflower oil gums contain approximately ~45% water, ~25% oil and ~30% phospholipids [6]. Therefore, the conventional alkaline process is a non-viable alternative to produce fatty esters from SOGs [1]. By contrast, the transesterification process by supercritical alcoholysis is an interesting option for this unconventional and low-cost feedstock [8]. In the supercritical technology, the alcohol and lipids, in a molar ratio of 40/1, are heated up to the reaction temperature (ca. 300 °C) in the absence of catalyst during ca. 20 min and under a pressure range of 100–200 bar [9]. Kusdiana and Saka [10] showed that the supercritical alcohol transesterification allows achieving high conversion even in the presence of water (up to 36 wt%) and fatty acids (up to 30 wt%) in the process.

In the present work, a three-variable factorial design of experiments was carried out to study the effects of temperature (280-320 °C), ethanol concentration (50–80 wt.%) and reaction time (20–50 min) on the supercritical ethanolysis. Then, a second statistical study was implemented at 280 °C to determine the effect of water content on the reaction yield (dehydration up to 35.0

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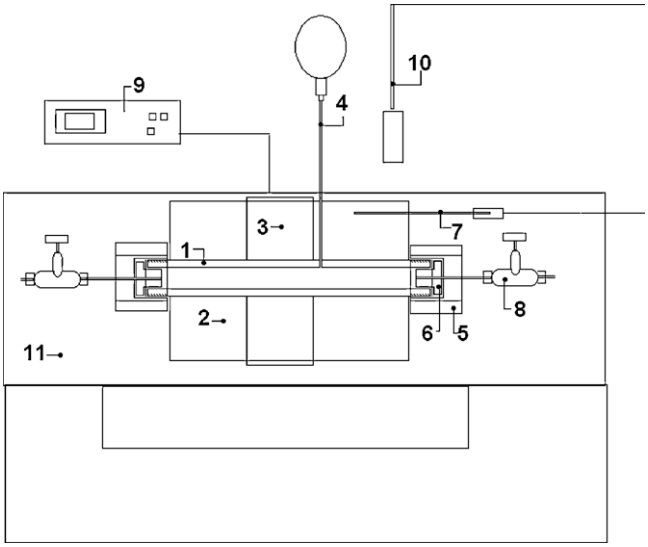

Fig. 1. Scheme of the batch reactor used for supercritical ethanolysis of SOGs. 1: High pressure stainless steel tube, 2: aluminum external jacket, 3: electric heat resistance, 4: pressure gauge, 5: retention screw, 6: seal system, 7: temperature sensor, 8: high pressure – temperature valves, 9: temperature controller, 10: nitrogen line (7 kg/cm^2), 11: isolated high temperature box.

and 2.4 wt% of water) while the ethanol concentration was fixed at 50 wt%.

2. Materials and methods

Sunflower lecithin sludges were provided by Oleaginosa Moreno Corp. (Bahía Blanca, Argentina). The chemicals used for the reaction and analysis were absolute ethanol (99.5%), pyridine (99.7%), hexane (98.5%), bis[trimethylsilyl]tri-fluoroacetamide (BSTFA, 98.6%), trimethylchlorosilane (TMCS, 97%), tetradecane (99%) and methyl heptadecanoate (99%) all purchased from Sigma–Aldrich except hexane which was bought from Cicarelli.

The supercritical ethanolysis of SOGs was carried out in a batch stainless steel reactor of 41 cm^3. Fig. 1 shows a scheme of the equipment. An electric resistance heater of 500 W connected to a temperature controller (Novus N480D) was used to heat the reaction cell. This cell was placed in an external aluminum jacket for homogeneous distribution of energy during the heating process. A Pt-100 platinum resistance thermocouple placed in the external aluminum jacket measured the temperature with an error of ±2 K. The pressure inside the reaction cell was measured by a pressure gauge (Dynisco PG4 serie), suitable for measurements at elevated temperatures with an error margin within 2%. The entire system was isolated with a fiberglass mat to reduce the loss of energy and to allow better temperature control.

The experimental procedure for carrying out the reactions was previously described elsewhere [5,11]. Basically, a given mass ratio of ethanol to gum was placed into the reactor at a global density of $\rho = 0.4$ g/cm^3. Once assembled, the system was heated up to the desired temperature, adjusting the power to obtain a heating rate of 10 K/min. During the controlled period (20–50 min) the rate of heating to keep the set point was decreased to 2 K/min and thereafter, the system was air-cooled to quench the reaction. After the reaction was finished, the excess of alcohol, water and any volatile product were evaporated with a nitrogen stream, and the mass of the products was gravimetrically determined.

The non-volatile products were divided in two fractions: hexane soluble and insoluble substrate. To this purpose, a sample of non-volatile products (~130 mg) was loaded into glass tubes with Teflon-lined screw caps and extracted with 25 mL of n-hexane. The tubes were centrifuged (5000 RCF, 30 min), and 8 mL of the upper solvent layer (i.e., the lipid products, LP) were transferred to a 10 mL vial and stored at −18 °C prior to GC-analysis. The solvent present in this sample was first evaporated under N_2 (60 °C drying temperature), and the LP fraction was weighted in a Sartorious CP 224S balance (±0.1 mg). Triglycerides and derivatives (fatty esters, fatty acids, mono and diglycerides) were identified by a GC/MS analysis, as were other relevant components in the reaction products. Standard calibration with perfluorotributylamine was performed following the protocol of TurboMass Software. On the other hand, the NIST MS Search Software [12] was used to identify compounds from their mass spectra by comparison with mass spectral libraries. The samples were prepared according to the GC-analysis protocol.

The esters content was determined by gas chromatography in a GC – Varian Star 3400 CX. The equipment was assembled with a flame ionization detector (FID) and capillary column (J&W Scientific, model DB-5ht, 15 m length, 0.32 mm inner diameter, and 0.10 μm film thickness). The chromatographic conditions were selected according to BS EN 14105:2003, modified to analyze FAEE, fatty acids, mono, di and triglycerides. Tetradecane was used as internal standard, and methyl heptadecanoate as a reference for fatty esters calibration. A stock solution of pyridine with a known amount of internal standard was prepared (~10 mg/mL). The sample injected to the chromatograph consisted of 2 μL of a solution prepared with 0.05 mL of the internal standard stock solution, 0.1 mL of liquid sample and 0.2 mL of silylating agent solution (BSTFA:TMCS 2:1 v/v).

Oil and lecithin content in the unreacted SOG samples were determined by quantification of acetone insoluble matter following the method used by Ceci et al. [13], based on the AOCS Official Method Ja 4-46. Hexane insoluble materials were determined according to AOCS Official Method Ja 3-87. Furthermore, the moisture content was analyzed by thermo-gravimetric analyses (Sartorious MA 35). Finally, the phospholipids profile was analyzed by high-pressure liquid chromatography (HPLC) following the approach of Hurst and Martin [14]. The HPLC flow rate was set to 1 mL/min to obtain a good separation of the peaks with a 5-min isocratic equilibration time between each loop injection of 10 mL. HPLC column calibration was performed using a standard mixture (purchased to Sigma, St. Louis, MO, USA.), containing 2.4 mg of L-a-phosphatidylethanolamine PE), 3.0 mg of L-a-phosphatidylcholine (PC), 1.8 mg of L-a-phosphatidylinositol (PI) and 0.6 mg LPC in 2 mL of chloroform solution.

The experimental evaluation of ester production by means of supercritical ethanolysis of SOGs was carried out by a statistical analysis according to a three-variable full factorial design of experiments with two replicates in order to estimate the experimental error [15]. Two response variables were studied: (i) lipid content in the reaction products, i.e., wt% of hexane soluble matter (Y_1) and (ii) the FAEE yield, defined as the mass fraction of fatty esters in the non-volatile reaction products (Y_2).

Two statistical studies were carried out. In the first, the effect of temperature (T), reaction time (t) ethanol concentration (E) were investigated when using the original SOG as raw material. The operating conditions were selected according to previous works on transesterification of vegetable oils with supercritical alcohols [8,9]. The temperature was set at 280 and 320 °C, the reaction was carried out during 20 and 50 min, and the initial ethanol concentration was set at 50 and 80 wt%.

As a consequence of the first study, a second statistical analysis was carried out at the mildest conditions, 280 °C and 50 wt% of ethanol in the feed, but a drying pretreatment at 70 °C was performed to the SOG in order to reduce its water content from ~50 to 35 and 2.4 wt%. The partial dehydration up to 35 wt% was selected according to a previous work [10] in which the effect of water was studied in the supercritical methanolysis of rapeseed oil. The

Table 1
Characterization of the SOG used in this work: moisture content, hexane- and acetone- insoluble material, lipid profile.

Moisture (g/kg)	Hexane-insoluble material (g/kg)	Acetone-insoluble material (g/kg)	Triglycerides (g/kg)
510 ± 40	4 ± 1	296 ± 62	190 ± 12

Phospholipids (chromatographic area, %)				Fatty acids (chromatographic area, %)	
PC	PE	PA	PI	C16:0–C16:1	C18:0–C18:1–C18:2
58	21	4	17	17	83

PC, phosphatidyl choline; PE, phosphatidyl ethanolamine; PA, phosphatidic acid; PI, phosphatidyl inositol; C16:0–C16:1, saturated and unsaturated fatty acids of C16, saturated and unsaturated fatty acids of C18.

Table 2
GC–MS analysis of the non-volatile and hexane-soluble fraction of reaction products. Retention time and relative composition of the products obtained in run N° 5.

Components	t_r (min)	A (%)
Ethyl palmitate	17.87	4.2
Hexadecanoic acid	18.43	7.6
Ethyl linoleate	19.77	21.6
Ethyl oleate	19.83	6.8
Ethyl stearate	20.08	1.2
Octadecanoic acid	20.55	27.1
Bis(2-ethylhexyl) adipate	22.00	0.5
Monopalmitin	23.60	13.1
Monolein	24.92	12.9
Diolein	28.72	3.8
β-Sitosterol	29.13	1.4

authors showed that a content of water up to 36 wt% almost does not affect the reaction yield. On the other hand, the mildest conditions were chosen for the second study to determine if the high water content in the raw material caused the poor performance of the reaction under these conditions, besides that these operating conditions are more promising from an economic point of view.

3. Results and discussion

3.1. Characterization of raw material and reaction products

Table 1 shows the characterization of the SOGs used in this work. This table reports initial moisture, hexane- and acetone-insoluble material, and lipids profile (fatty acids and phospholipids). Hexane insoluble materials are solid impurities considered as an inert substrate in the reaction. On the other hand, the phospholipids and triglycerides fractions are given by the acetone insoluble and soluble substrate, respectively.

The non-volatile fraction of the reaction products was analyzed by GC–MS (Table 2) and HPLC to evaluate which oily components remained in the mixture. Neither the triglycerides nor the phospholipids, initially present in the raw material, were found in the reaction product, indicating that they were completely converted.

Table 4
Statistical analysis of the experimental runs. Average value of the response variables, main effects of the studied variables and their quadratic interactions.

	Hexane soluble products (Y_1%)	FAEE yield (Y_2%)
Average	77 ± 1	41 ± 1
Main effects		
Temperature (T)	2 ± 2	14 ± 2
% Ethanol (E)	5 ± 2	11 ± 2
Reaction time (t)	−2 ± 2	8 ± 2
Two factor interaction		
$T \times E$	2 ± 2	2 ± 2
$T \times t$	−1 ± 2	−4 ± 2
$E \times t$	−4 ± 2	2 ± 2

The main components identified according to the GC–MS analysis were ethyl esters and free fatty acids. Also, monoglycerides and diglycerides were detected but in minor quantities.

3.2. Direct supercritical ethanolysis of SOGs

The results obtained according to the three-variable full factorial design of experiments are summarized in Table 3. In general terms, the results show that the hexane-insoluble material increased after each experimental run, from ∼0.4 wt% in the original SOG up to ∼20 to 25 wt%. On the other hand, the maximum FAEE yield was ∼55 wt%. It is important to highlight that, due to the presence of phospholipids, the theoretical maximum mass yield of esters that could be achieved, if all the lipids present in the samples were converted to *FAEE*, was estimated as 87 wt%.

Table 4 shows the effects on the response variable, hexane soluble material (Y_1%) and the FAEE yield (Y_2%), of temperature, ethanol concentration and reaction time, as well as the quadratic interaction of these variables. The standard deviation calculated from the statistical design and the two replicates is also reported [15].

The average value of the hexane soluble reaction products (Y_1 = 77 wt%), obtained from the experimental runs, is a representative outcome with interval boundaries for this response variable of 72 wt% < Y_1 < 83 wt%. From the statistical analysis, the temperature and reaction time did not have significant influence on Y_1 in the experimental range studied in this work. According to the deviations, their effects are not statistically greater than the uncertainties associated with their determination. On the other hand, the ethanol concentration showed a minor effect on this response variable with a positive effect ($E = 5 \pm 2$). The increase of hexane soluble fraction with the concentration of ethanol in the system is related with the partial miscibility of triglycerides/phospholipids in ethanol at temperatures lower than 130 °C [16]. The lipids were in direct contact with the reactor wall during the beginning of the heating period, which is longer in the case of feeding less amount of ethanol.

On the other hand, the three variables had an important effect on the production of FAEE from SOG with supercritical ethanol (response variable Y_2). The temperature was the most important of these variables with a positive effect ($T = 14$); an increase of the final reaction temperature in the supercritical process produced

Table 3
Experimental runs of direct alcoholysis of SOGs (average of two replicates).

Run	T_f (°C)	Ethanol (wt%)	t_f (min)	Water/EtOH (molar basis)	P_f (bar)	Y_1%	Y_2%	FFA%
1	280	50	20	1.3	70	72.4	22.8	49
2	320	50	20	1.3	120	75.8	42.2	37
3	280	80	20	0.3	82	80.2	32.6	24
4	320	80	20	0.3	136	82.5	50.9	16
5	280	50	50	1.3	70	80.8	37.4	51
6	320	50	50	1.3	120	77.9	41.9	39
7	280	80	50	0.3	82	75.6	43.4	21
8	320	80	50	0.3	136	79.2	55.3	13

Y_1, hexane soluble reaction products; Y_2, FAEE yield; FFA, free fatty acids relative content ($area_{FFA}/(area_{FFA} + area_{FAEE})$).

Table 5
Influence of drying pretreatment in the supercritical ethanolysis of SOGs.

Run N°	T_f (°C)	t_f (min)	Water(wt%)	P_f (bar)	Y_1%	Y_2%	FFA% = FA/(FA + FAEE)	Water/EtOH(molar basis)
1	280	20	35.0	84	80.7	42.3	25	0.9
2	280	50	35.0	84	78.8	46.9	25	0.9
3	280	20	2.40	70	82.2	51.4	9	0.1
4	280	50	2.40	70	73.9	51.0	9	0.1

a significant increment in the FAEE yield. The statistical deviation and the quadratic interaction ($T \times E$, $T \times t$ and $E \times t$) had nearly the same values, indicating that the quadratic interaction effects were negligible in the process, from the statistical point of view.

Fig. 2 shows the FAEE yield as a function of the reaction time for the initial ethanol concentrations (50 and 80 wt%) and both studied reaction temperatures (280 and 320 °C).

An increase of ethanol concentration and temperature enhanced the FAEE yield. Indeed, the effect of ethanol concentration was more important at the highest temperature, in which an initial charge of 80 wt% ethanol produced a 55% yield toward FAEE.

The temperature effect on vegetable oils transesterification with supercritical alcohols was previously reported by several authors [8,9]. For example, Valle et al. [5] showed that the supercritical ethanolysis of *Raphanus sativus* L. oil (reaction time of 15 min and an ethanol to oil molar ratio of 42) achieved a 95% FAEE yield at ~325 °C, while at lower temperatures (~300 °C) the FAEE yield diminished to 72%. These observations are in agreement with results reported in this work.

Furthermore, the molar ratio of alcohol to oil also affects the reaction. In practice, an excess amount of alcohol is usually used to drive the reversible reaction toward the products side and get more FAEE. Pinnarat and Savage [9] showed that increasing the molar ratio of alcohol to oil produced a significant enhance in the final ester content. Moreover, Bunyakiat et al. [17] found that the conversion was nearly doubled when the alcohol to oil molar ratio was augmented from 6 to 42 in the transesterification of coconut oil and palm kernel oil. Higher ethanol to lipid ratio also reduces the critical temperature of the mixture, which allows achieving homogeneous reaction conditions at milder temperatures. Hegel et al. [18] showed that the critical temperature of mixtures of triglycerides and alcohols decreased from 325 to 300 °C when the molar ratio of alcohol to vegetable oil increased from 40 to 50. Therefore, as more alcohol is fed, higher conversions can be obtained, but eventually a point is reached where more alcohol hinders the reaction kinetics, due to the lipid dilution in the reactants mixture [18]. In this work, an increment of ethanol concentration from 50 to 80 wt% produced an enhancement in the FAEE content, which was higher at 320 °C.

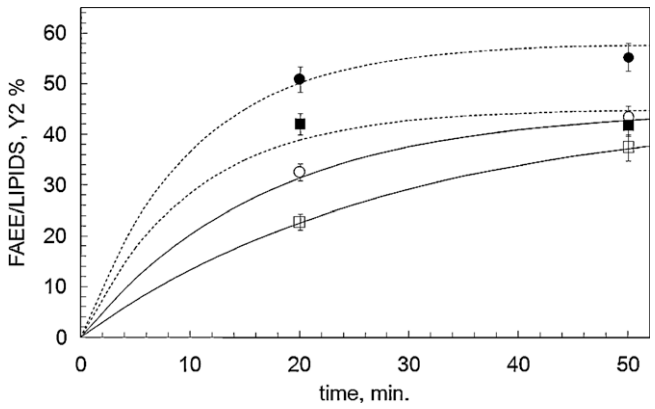

Fig. 2. FAEE yield at different temperatures and ethanol to gum mass ratio. Experimental data: solid symbols 320 °C ((●) 80 wt% and (■) 50 wt%) empty symbols at 280 °C ((○) 80 wt% and (□) 50 wt%). Lines: sketched for better visualization of FAEE yield trend with operating conditions.

3.3. Effects of water and SOG dehydration

The raw lecithin contains nearly 50 wt% water, which plays an important role in the reaction. Previous works showed that the presence of water does not hinder the supercritical transesterification reaction as it does in the catalyzed synthesis [10]. However, a content of water as high as 50 wt% was not evaluated. On the other hand, in this work, a high content of free fatty acid was found in the reaction products. Table 3 shows the relative area (A, %) of free fatty acids to FAEE measured in the product samples.

In general, the lower the FAEE yield, the greater the fatty acids concentration in the products. Table 3 shows that the content of fatty acids increased at 280 °C, and this increment was even more significant for the ethanol concentration of 50 wt%. Table 3 also reports the initial water to ethanol molar ratio. As can be seen, those runs with high water to ethanol ratio resulted in a final product with higher fatty acids content.

Since the esterification reaction is also reversible, the presence of water pushes backwards the FAEE yield. Therefore, a drying pretreatment of the raw sludge may be advisable to promote the esterification reaction. The original sunflower wet sludge was subjected to a drying process at 70 °C in a vacuum oven to reduce the water content of the material to be processed in the supercritical ethanolysis. Two degrees of dehydration were studied, a partial dehydration up to 35 wt% of water and nearly complete drying up to 2.4 wt%. On the other hand, the ethanol content was kept constant at the lower value (50 wt%), which means that the ethanol to lipids molar ratio (ELR) was also reduced. When there is 35 wt% of water in the SOG, the ELR was 28, while for dehydrated SOG (2.4% humidity), the ELR was 19. As we already mentioned, according to previous results published in the literature, the lower the molar ratio, the lower the yield toward esters [8,9]. Table 5 shows the results of the two variable full factorial design of the performed experiments in which the ethanol concentration and temperature were set at 50 wt% and 280 °C, respectively.

As can be seen in Table 5, the content of free fatty acids in the reaction products was lower in comparison with the previous results, when the water content of the raw material was about 50 wt%. This is more significant in the dehydrated SOG (2.4 wt% humidity), even though in this case the ELR is lower. The reaction products soluble in hexane (Y_1%) have a similar behavior with respect to the previous experiments. The mean value of hexane-soluble material was 79 wt%, and both, the water content and the reaction time, had a low negative influence on it (Table 6).

Table 6
Statistical analysis of the experimental runs with drying pretreatment. Average value of the response variables, main effects of the studied variables and their quadratic interactions.

	Hexane soluble material (Y_1%)	Fatty acid esters yield (Y_2%)
Average	79 ± 1	48 ± 1
Main effects		
Reaction time (t)	−4 ± 2	3 ± 2
Water content (W)	−4 ± 2	5 ± 2
Two factor interaction		
$t \times W$	1 ± 2	0.3 ± 2

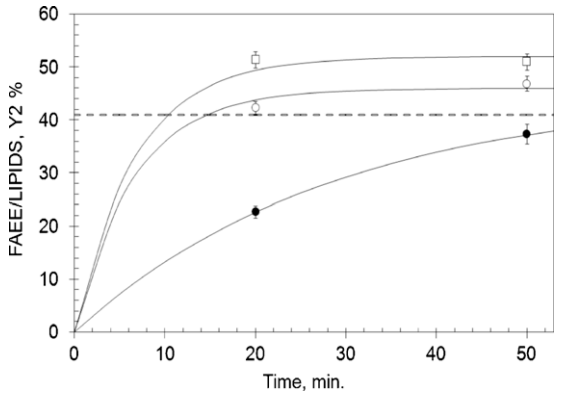

Fig. 3. FAEE yield of reactions carried out at 280 °C and 50 wt% of ethanol. Experimental data: (□) 2.4%, (○) 35%, (●) 50% of water content. Solid lines: sketched for better visualization of FAEE yield trend with operating conditions. Dashed line: maximum FAEE yield if only the triglycerides of the SOG were recovered.

The analysis of ester content in the reaction products shows that the pretreatment to remove water produced an increment of FAEE yield, the mean value of fatty acid ester was 48%, even though only experiments at low temperature (280 °C) were performed (Table 6).

Fig. 3 shows the influence of the drying pretreatment in the reaction. It depicts the FAEE yield against time at 280 °C for the three different water contents studied in this work. After the drying pretreatment the FAEE yield was almost constant between 20 and 50 min of reaction time. Consequently, according to the statistical effects (Table 6), this variable showed a low influence in the ethanolysis of SOGs because a reaction time of 20 min is enough to get the maximum FAEE yield at 280 °C. The most important factor for the response variable Y_2, was the water content in the system (W = 5, Table 6), whose reduction caused an increase in the FAEE yield. The effect of water becomes more evident when the results are compared with the previous runs at 280 °C and SOG with nearly 50 wt% of water content (see Fig. 3). For example, at a reaction time of 20 min, the FAEE yield was 23% for the original SOG, while a partial dehydration up to 35 wt% produced an increase of the FAEE yield up to 44%.

Given the high water content in the raw material, the water to lipids molar ratio (WLR) in the system was about 46 in the ethanolysis of the original SOG. On the other hand, as was already mentioned, the ELR was 35 when 50 wt% of ethanol was fed, which is lower than the WLR and led to a high free fatty acid content in the reaction products (Run N° 1, 2, 5 and 6 reported in Table 3). The drying process reduced the WLR promoting the conversion of the lipids toward fatty esters.

Besides equilibrium conversion, water removal also enhanced reaction kinetics. Figs. 2 and 3 show that similar rates were achieved at 280 °C with dehydrated SOG, and at 320 °C without the drying step; i.e., ca. 50% yield in 20 min. Similar behavior shows the transesterification of triglycerides in the presence of water [10].

While the drying process enhances the production of esters, it also represents a higher capital cost for the process. Nevertheless, it can contribute to reduce the energy consumption since the reaction is carried out at a higher temperature than that required to evaporate water. Moreover, the pretreatment also allows reducing the ethanol to oil ratio, which indeed contributes to mitigate the operating cost as well.

Finally, Fig. 3 also shows the maximum theoretical yield if only the neutral lipids (triglycerides) were reacted (dashed line at almost 40%), which is lower than the achieved yield. The aim of this work was to recover that fraction of occluded oil; however, part of the fatty acids coming from the polar lipids (phospholipids) were also recovered in the process. It is important to highlight that, although lecithin is a high value added product, the actual production is far over the market requirements.

4. Conclusions

Fatty acid ethyl esters (FAEE) were produced by supercritical ethanolysis of vegetable oil sludges. According to the experimental results shown in this study, the reaction behaves similar to the corresponding transesterification of triglycerides. Therefore, the ethanol concentration and temperature have a positive effect on the production of FAEE, the latter being more evident at the highest ethanol concentration.

When 50 wt% of ethanol was fed to the reactor, the final FAEE yield was about 40% for the both studied temperatures. However, in the case of 80 wt% of ethanol in the feed, the final yield increased up to 55% at the higher temperature. Moreover, the presence of water in the system promotes the backwards reaction toward free fatty acids. After a drying pretreatment of the raw material, a yield of 49% toward FAEE was achieved carrying out the reaction during 20 min at 280 °C and with 50 wt% of ethanol.

The drying pretreatment allows processing more raw material per reactor unit of volume and achieving better yields under milder conditions. Further work is required to locate the optimum water and ethanol content, since both affect the equilibrium conversion and the reaction kinetics. The most remarkable conclusion of this work is that supercritical alcoholysis is a simple technology to recover valuable products from oily sludges.

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