J. of Supercritical Fluids 79 (2013) 62–66

Contents lists available at SciVerse ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Fatty acids recovery from vegetable oil wet sludge by supercritical alcoholysis

G. Soto, A. Velez, P. Hegel, G. Mabe, S. Pereda*

PLAPIQUI, Universidad Nacional del Sur - CONICET, CC 717, 8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:
Received 5 July 2012
Received in revised form 11 January 2013
Accepted 12 January 2013

Keywords:
Phospholipids
Triglycerides
Fatty acids
Sludge
Supercritical
Alcoholysis

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.

© 2013 Elsevier B.V. All rights reserved.

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

* Corresponding author. Tel.: +54 2914861700; fax: +54 2914861600.
E-mail addresses: spereda@plapiqui.edu.ar, spereda@gmail.com (S. Pereda).

0896-8446/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.supflu.2013.01.003

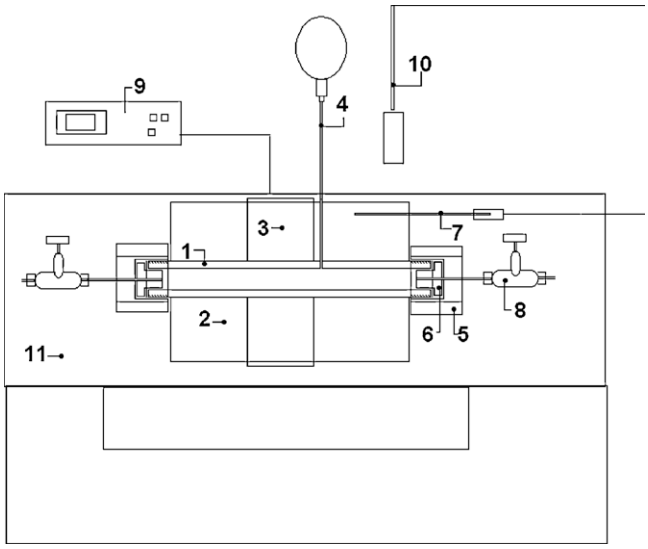

Fig. 1. Scheme of the batch reactor used for supercritical ethanolysis of SOGs. 1: High pressure stainless steel tube, 2: aluminum external jacket, 3: electric heat resistance, 4: pressure gauge, 5: retention screw, 6: seal system, 7: temperature sensor, 8: high pressure – temperature valves, 9: temperature 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

Download English Version:

https://daneshyari.com/en/article/230715

Download Persian Version:

https://daneshyari.com/article/230715

Daneshyari.com