J. of Supercritical Fluids 110 (2016) 83–89

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Cosolvent effect on the recovery of triglycerides from used frying oil with modified supercritical ethane

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ARTICLE INFO

Article history:
Received 7 October 2015
Received in revised form
11 December 2015
Accepted 14 December 2015
Available online 17 December 2015

Keywords:
Supercritical extraction
Ethane
Cosolvent
Solubility
Selectivity
Used frying oil
Triglycerides

ABSTRACT

Supercritical extraction with modified ethane was used for the separation of triglycerides from waste frying oil in a semicontinuous system. Cosolvents used to modify pure solvent behavior were ethanol, methanol, acetone, and hexane. They were selected because of their different capacity to form hydrogen bonds. The effect of cosolvent type on extraction yield and oil solubility followed the order: ethanol > methanol > acetone > hexane. However, their efficiency to separate triglycerides from polar species showed the opposite trend: ethanol < methanol < acetone < hexane. Regarding the effect of cosolvent concentration, yields and solute solubilities increased with increasing values of the variable. However, the separation efficiency was almost independent of cosolvent concentration. Finally, the extraction process was further analyzed in a continuous packed column. At the best conditions 95% of triglycerides were recovered, being the polar content of the extract only slightly higher than of the fresh oil.

1. Introduction

Used frying oil is the waste that remains after fresh frying oil degradation occurs due to its repeated use in several frying processes. It mainly consists of triglycerides (about 70% by weight) and the products of oil degradation: free fatty acids, mono- and diglycerides, oxidized triglycerides, and oligomeric triglycerides or polymers [1].

Waste frying oils are generally discarded because these oxidized lipids degrade the quality of fried foods. However, since the discarded used-frying oil still has a large portion of non-degraded triglycerides, economic considerations have stimulated the interest in its purification [2,3].

The separation of non-degraded triglycerides from undesirable oxidized polar compounds may be accomplished by using supercritical fluid extraction [4–6]. The main advantages of this technique are: high speed, high selectivity tunable with single changes in operation pressure and/or temperature, energy savings regarding solvent removal, cleanness and environmental-friendliness [7,8]. However, we should not forget some drawbacks: costs in gas compression and confinement, and smaller solute solubilities in high pressure solvents in comparison to conventional solvents [9]. Nevertheless, the low solubility problem may be solved by using solvent modifiers or cosolvents [10,11].

In this context, our research group has already reported the study of the triglycerides recovery from used frying oil with supercritical CO_2 and some hydrocarbons as ethane and propane [12,13]. Moreover, the use of cosolvents to increase the solvent powers and selectivity of CO_2 has also been investigated [14,15]. All these works have evidenced that the supercritical fluid extraction can be a competitive technology for regeneration of frying waste oil, although a bigger effort has to be done in order to improve the results obtained.

Considering that hydrocarbon solvents such as ethane and propane have been reported to be better solvents for lipids than CO_2 [10,12,13] and that their behavior can be enhanced by adding small amounts of cosolvents [10,14,15], in this work four substances have been tested as cosolvents (ethanol, methanol, acetone, and hexane) to improve the efficiency of pure ethane in separating the triglyceride fraction from the used frying oil. Therefore, the specific objective of this work will be to establish the cosolvent effect on both extraction yield and efficiency of the modified solvents to separate non polar triglycerides from the undesired polar fraction of the oil. Then, according to results obtained, the best cosolvent is selected. Moreover, with the purpose of smoothing the way for the industrial implementation of the process, the continuous

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http://dx.doi.org/10.1016/j.supflu.2015.12.008
0896-8446/

Table 1
Composition of sunflower frying oil: fresh, used, and recovered.

	Fresh oil	Used oil	Extracted oil
Non-polar compounds (%)	92.7	70.1	89.0
Polar compounds (%)	7.3	29.9	11.0
HMWC[a]	3.4	13.0	1.7
Polymers	1.1	4.7	–
Dimers	2.3	8.3	1.7
LMWC[b]	3.9	16.9	9.3
Oxydized triglycerides	3.0	12.9	8.5
Diglycerides	0.6	2.8	0.7
Fatty acids and others	0.3	1.2	0.1

[a] HMWC: polar compounds with higher molecular weight than triglycerides.
[b] LMWC: polar compounds with lower molecular weight than triglycerides.

fractionation of the oil is analyzed in a packed countercurrent column and the best solvent-to-oil ratio is determined. Ethane modified by the selected cosolvent (hexane) has been used to perform the continuous extraction.

2. Experimental procedures

2.1. Materials

Liquid ethane (purity 99.4%) was supplied by Praxair (Spain). Methanol, ethanol, acetone, and hexane, all of them HPLC grade, were supplied by Sigma Aldrich (USA).

Fresh frying oil was refined sunflower oil provided by Diasol (Borges, Spain). Frying-waste oil was obtained from fresh oil by heating it for 14 h at 195 °C in a frying machine. This fried oil was stored at 0 °C in hermetic bottles, in the dark, and in a N_2 atmosphere (to avoid further oil degradation because of oil contact with oxygen, light, or humidity). It has been reported in the literature that oil degradation by heating is similar to that obtained in true frying processes regarding parameters such as the percentage of polar compounds and conjugated diolefines [1,16]. Table 1 summarizes the composition of the fresh and used sunflower frying oil. They were determined following the analytical procedure described in [17] and outlined below.

Finally, chemicals used for oil characterization were: Petroleum ether (Panreac, Spain), diethyl ether (Panreac, Spain), silica gel (Merck, USA), sea sand (Panreac, Spain), diisopropyl ether (Fisher Scientific, USA), oleyl-rac-glycerol (Sigma Aldrich, USA), tetrahydrofuran (Panreac, Spain), and cyclohexane (Panreac, Spain).

2.2. Apparatus and extraction procedure

Semicontinuous experiments were performed in the extraction apparatus schematically shown in Fig. 1 and detailed described in the literature [18]. Briefly, it works as indicated below. Liquid solvent from a stainless-steel cylinder (SC) was cooled (CS), filtered (F), and compressed by a membrane pump (P1) (HG-140, LEWA, Germany). The pressure was regulated by a backpressure regulator (BPR) (BP-66, GO Regulator, USA) and checked by a manometer (M1). Cosolvent was pumped into the system using a high pressure pump (P2) (PU 2086 Plus, JASCO, USA). The compressed modified solvent was passed through the extractor (EX), a 940 cm^3 stainless-steel cylinder loaded with used frying oil (50 g). To keep the extractor temperature at the desired value, it was submerged into a thermostatic bath with mineral oil. The oil-laden gas from the extractor was passed through a heated metering valve (MV) where the pressured solvent was expanded, and the extracted oil and solvent separated. The extracted oil was collected in a receiver at ambient temperature (RE1) and the cosolvent in a second receiver at 0 °C (RE2). The gas flow through the extractor (4 L/min) was measured with a flow meter (FM). Extracts recovered in receiver RE1 were heated at 60 °C for 60 min in order to eliminate any cosolvent that could contaminate the oil. The oil collected was gravimetrically quantified and properly stored for further analysis. The solvent leaving the system was burned. Finally, it should be noted that at the operating conditions of this work ethane was completely miscible with all cosolvents tested [19–23], a fact that should always be considered in order to ensure the desired cosolvent effect. To minimize experimental errors all runs were replicated twice. Extraction yields of replicates differed about 1%.

The continuous installation is basically similar to the semicontinuous apparatus described above [12]. Specifically, the most significant difference is that, in the case of the continuous system, the section within the dotted line boundary of Fig. 1 is substituted by elements shown in Fig. 2. Namely, a high pressure pump (P3) (PU 2080 Plus, JASCO, USA), a jacketed packed column, and a storage drum (SD). The column was made of AISI 316 stainless steel and had a total height of 170 cm and a volume of 2.14 L. It consisted of three jacketed cylinders 50 cm long and 2 cm inside diameter each. The wall temperature of each cylinder was maintained at ±0.5 °C by using water baths. The storage drum (SD) had 1-L volume and was used to collect the non dissolved oil fraction (raffinate). It was changed periodically (every 2 h) to prevent column flooding. When operating in this system, at the beginning of the run and before the feed was introduced, the column was allowed to equilibrate thermally for about 1 h. Then, an oil volume equal to the void space in the bottom cylinder was pumped in. Next, the modified solvent was introduced into the column at the desired operating pressure. The pressurized column was then equilibrated for 1 h before the metering valve (MV) was opened. Once opened this valve (MV) the

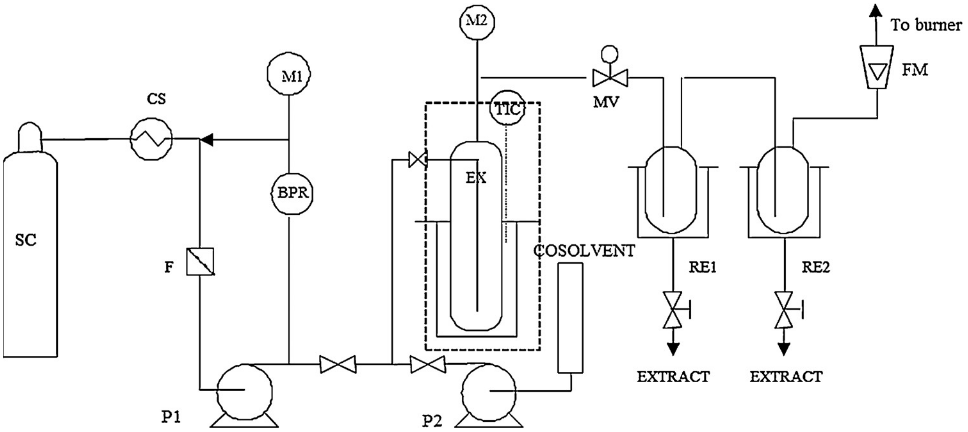

Fig. 1. Flow diagram of the semicontinuous extraction set-up.