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Volatile oil isolation by continuous supercritical extraction

Introduction

Majority of valuable seed oils are already produced commercially using supercritical fluids and supercritical CO_2 extraction technology. Researches are focused on the separation of such components as polyunsaturated fatty acids, carotenoids, phospholipids and volatile oils.

Recently, the extraction of essential oil components using a solvent at high pressure or supercritical fluids received much attention, especially in food, pharmaceutical and cosmetic industries, because it presents an alternative to conventional processes such as organic solvent extraction and steam distillation [1, 2]. Supercritical fluid extraction (SFE) enables a continuous modification of solvent power and selectivity by changing the solvent density [3, 4].

The fractionation of polyunsaturated fatty acids to produce concentrates have had limited commercial success in spite of extensive research that has been carried out in this area [4]. High value seed oils produced by cold pressing or supercritical extraction have usually high content of volatile oils, which could easily be lost during further processing. The value of volatiles depends on difficulty in isolation and preservation while processing with conventional technologies.

In the framework of research methods of the volatile fraction isolation of *Nigella sativa* oil were proposed. The seed yields volatile oil containing thymoquinone, melanthin, nigilline, damascene and tannin. The volatile oil and its main active constituent, thymoquinone, inhibits infection, relieves pain, stimulates gall bladder and works as an antioxidant [5].

Nigella sativa oil is usually produced by a hot solvent extraction method at 40-60°C and even at 70°C [6]. The hot extraction method can affect oil properties and may induce partial alteration of the majority of minor constituents that are responsible for essential functions of the product. The use of *Nigella* seed oil for industrial applications could necessitate its exposure to high thermal treatments that could lead to changes in quality characteristics of the oil [7].

Continuous column extraction of model high value seed oil (rapeseed oil and thymoquinone solution) was carried out to establish the possibility of volatile oil separation from supercritically extracted oils. The aim of this study was to determine the continuous supercritical oil extraction as an effective method for volatile fraction separation, and to investigate the effect of operating conditions on the extract yield and separation efficiency. Such data would facilitate the estimation of process parameters for full-scale separation of oil and its volatile components.

Experimental

Extraction column

A laboratory fractionation column was built and used for extraction experiments (Fig. 1). The column consists of three 0.5 m and two 0.25 m long sections which are connected by cross or tee fittings. Each section is heated by wire heaters wrapped around the column wall and connected to a PID separate temperature controller (T-202, *Czaki*, Poland), equipped with a thermocouple (type K) placed in the column at the end of each section.

Column parts are made of AISI 316 stainless steel and are designed to withstand maximum internal pressure of up to 30 MPa at 60°C. The column is packed with wire mesh and thermally insulated with glass wool. The required temperature gradient along the column is maintained by an independent temperature control in each section. The lines for feed streams, CO_2 introduction and products are attached to the column at the section connection fittings. The sampling line is connected to the top of the column to collect extract. The sampling line contains an on/off valve and metering valve for manual control of the flow rate. A pressure gauge is used at the top of the column to monitor column pressure. A *Jasco PU2080* pump (P1) was used to deliver CO_2 continuously to the column from the bottom zone.

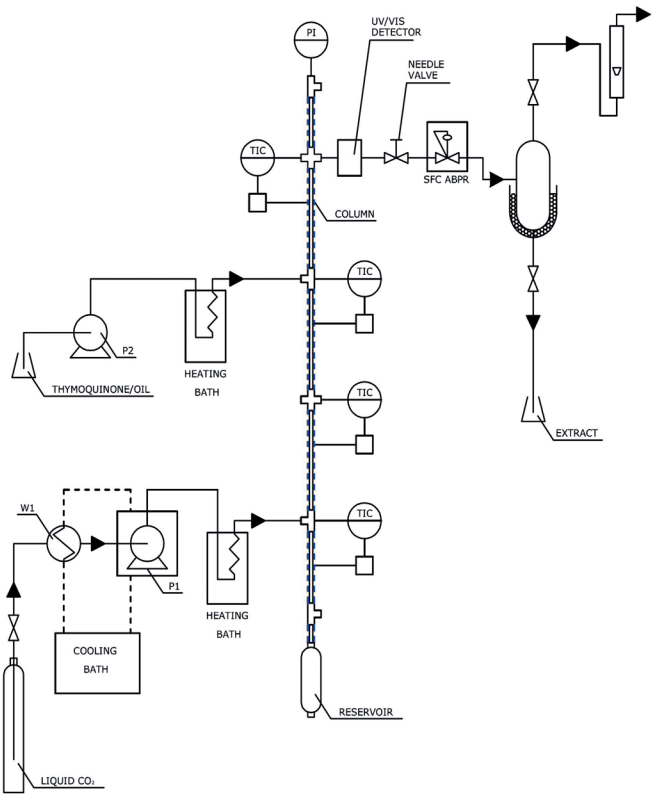

Fig. 1. Schematic of experimental SFE apparatus

The thymoquinone/oil mixture was withdrawn from a reservoir and fed to the column through heating bath by a high-pressure piston *Waters* M 510 pump (P2). In all experiments the mixture of oil and thymoquinone was fed to the column at 0.3 ml/min flow rate. The concentration of thymoquinone at the outlet was monitored with a *Jasco* UV970M detector.

Thar Instruments SFC ABPR 20 restrictor was used to reduce pressure to an ambient level. Low-pressure CO_2 was separated from the thymoquinone extract by a cooled separator. Ahead of the vent, the flow rate and total quantity of CO_2 used were measured by a rotameter. To stabilize temperature and pressure in the column, the system was heated for at least 1 h to reach the required process parameters. Next, CO_2 was pumped to the bottom of the column at a constant flow rate. After the next 20 minutes the oil mixture was pumped into the upper section of the column. Since then the thymoquinone concentration before BPR was traced by a UV/VIS detector.

Steady state conditions were reached usually after half an hour. The extraction lasted for the next two hours, then it was stopped, and collected products were analyzed. The parameters of all experiments are given in Table 1.

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Tab 1. Experimental conditions

Experiment number	Pressure	Temperature	CO_2 density	CO_2 flow	CO_2 flow/oil flow
	MPa	°C	kg/m^3	g/min	m^3/m^3
#1_100/20	10	20	855.32	2.242	6.354
#2_100/20	10	20	855.32	2.242	6.354
#3_100/40	10	40	615.42	2.242	8.831
#4_150/20	15	20	904.43	2.242	6.001
#5_150/40	15	40	780.70	2.242	6.961

In all presented experiments temperature was the same along the extraction column except the last 50 cm long section where the temperature was risen by 5°C in order to reduce the solvent density.

Materials and methods

The solution of thymoquinone in rapeseed oil was used as a model of black cumin oil, as it has been mentioned before. Commercial rapeseed refined oil from *ZPT Kruszwica*, Poland was used without any further purification. Thymoquinone purchased from *Aldrich* ($C_{10}H_{12}O_2$, purity 99%, 274666, Germany) was used without further purification. Pure CO_2 (99.9%) was purchased from *Air-Liquid* (Lodz, Poland).

Model mixtures of thymoquinone and rapeseed oil were made to simulate the black cumin oils of cold pressed or supercritically extracted black cumin oils with high content of thymoquinone, which is a predominant constituent of the volatile fraction [8]. The concentration of thymoquinone in the black cumin oils does not exceed 0.5%. For the purpose of the present experiments the thymoquinone solution in the rapeseed oil was prepared with the final concentration of 0.41%. The concentration of thymoquinone at the outlet was traced on-line with a UV/VIS detector at 655 nm and 295 nm wavelength simultaneously.

Results and discussion

Recovery of thymoquinone

Thymoquinone separation at steady-state extraction with CO_2 was tested. The mixture of rapeseed oil containing 0.41% thymoquinone by weight was used as a model of black cumin oil. Only above 40°C and at pressures above 15 MPa these compounds have significant solubility in supercritical CO_2. Some authors presented literature review of experimental data on triglycerides that confirm this general trend [9, 10]. Consequently, to test separation of oil and volatile fraction modeled with thymoquinone, several experiments at 20°C, 40°C and pressure 10MPa, 15 MPa were performed. As the rapeseed oil is virtually insoluble up to 150 bar it was assumed that the best conditions for the separation process were below 15 MPa and 40°C.

Results of the extraction experiments on rapeseed oil and thymoquinone separation are illustrated in Fig. 2a and Fig. 2b and parameters of separation tests are given in Table 2.

Tab 2. Recovery data of thymoquinone and rapeseed oil separation tests

Experiment number	Thymoquinone concentration measured with UV/VIS detector	Apparent yield	Collected extract
	ppm	%	mg
#1_100/20	433.7	0.86	102.2
#2_100/20	429.1	0.85	94.6
#3_100/40	409.5	0.81	69.0
#4_150/20	448.9	0.89	101.8
#5_150/40	418.9	0.83	84.6

Apparent yield was calculated as a product of thymoquinone concentration measured with the UV/VIS detector and CO_2 flow. As the scale of the experiments was small, the apparent yield exceeded the amount of extract collected in a hexane cold trap.

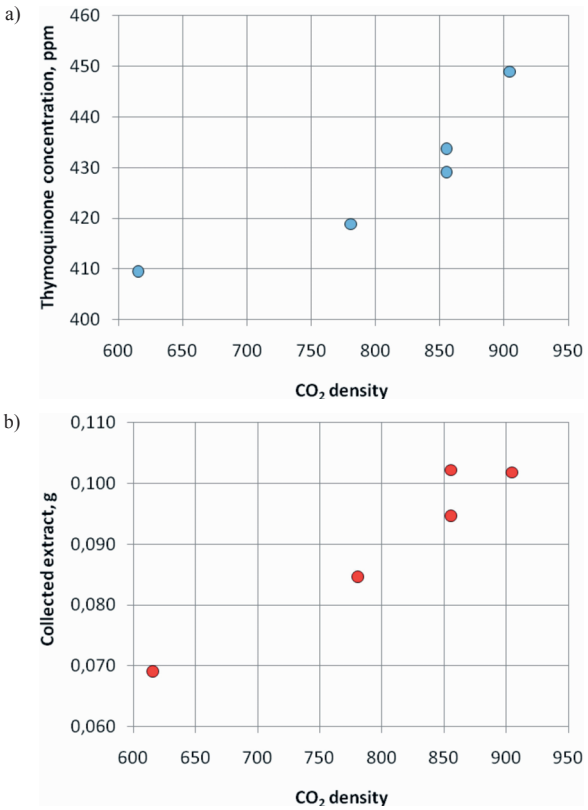

Fig. 2. a) Thymoquinone concentration in a CO_2 stream leaving the extractor, b) Collected extract versus CO_2 density

The concentration of thymoquinone in the CO_2 stream at the outlet of the column was less than 500 ppm, but it was high enough to reduce thymoquinone concentration in the oil by factor 10.

Conclusions

The results suggest that the separation of thymoquinone (volatile oil) from crude oil is possible by means of supercritical extraction. The SFE method offers important advantages over hydrodistillation, namely separation in oxygen-free environment, low temperature safe for sensitive components and short extraction time. Also the cost of SFE is not higher than for other separation methods (energy cost is fairly higher to perform hydrodistillation than that required to reach supercritical conditions). The method contributes to the automation of food industry.

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