Prosimy cytować jako: Inż. Ap. Chem. 2012, 51, 6, 322-323

Karina GURGENOVA, Paweł WAWRZYNIAK

e-mail: karina@wipos.p.lodz.pl

Department of Heat and Mass Transfer, Faculty of Process and Environmental Engineering, Lodz University of Technology, Poland

Batch high-pressure supercritical fluid extraction of essential oil from black cumin seeds

Introduction

The black cumin (*Nigella Sativa* Linn.), also named as Roman coriander, kalonji or nigella, orginate from south and southwest Asia and has been cultivated in the tropics, subtropics and temperate regions like central Europe on a large scale. The seeds of black cumin have length about 0.3 cm each, and have black colour. The seeds are used for their strong smell and bitter tasting flavour in sweets, alcoholic beverages and as whole seeds on bread. [*Paarakh, 2010*]. In addition, Nigella fixed oil and its volatile oil are used in the pharmacy and cosmetics industry. Depending on the way and the region of cultivation, Nigella seeds contain more than hundred different volatile components. Primary component of volatile fraction is thymoquinone [*Khan, 1999*]. Thymoquinone is a biologically active component, and is used for the treatment of many different illnesses, such as diarrhea, bronchial asthma and as a cancer therapy [*Khan, 1999; Wajs et al., 2008*]. Despite the extensive studies, there are still many components in black cumin seed that have not been identified.

The edible oil is conventionally extracted by the mechanical cold-pressing process or solvent extraction. The properties of oil extracted by the mechanical press process are better, since oil is not contaminated with any chemical, but the yield of this process is low [*Brunner,1994*]. The output and extraction rate are higher using solvent extraction but in conventional solvent extraction methods, solvent is mixed with oil and during post processing, a lot of valuable volatile components are easily lost. Supercritical carbon dioxide (SC-CO_2) extraction of the edible oil has attracted high attention as a sustainable alternative to conventional solvent extraction and cold-pressing process. The main reason to use that technology is that SC-CO_2 not only has a higher extraction rate but also is a non-toxic, non-explosive, non-flammable, readily available solvent, which is easy to remove from the extracted materials. The extract quality can also be controlled, and storage capability of extract can be extended [*Weinhold et al., 2008*].

Some authors have done supercritical fluid extraction of Nigella seeds at the conditions of 150÷200 bars and 308, 318 K with gas flow rate range of $0.6\div1.2\cdot10^{-6}$ m^3/s [*Fullana et al., 1999*; *Wawrzyniak et al., 2003*].

Results of batch supercritical carbon dioxide extraction of black cumin seeds are presented. The influence of extraction conditions on yield and volatile oil composition of black cumin seeds is discussed.

Materials and methods

Materials

Black cumin seeds were supplied by *Sasa*, Germany, and were used without further purification. Pure CO_2 (99.9%) was purchased from *Air-Liquid* delivered at pressure up to 60 bar.

Batch Extraction

The solid-liquid batch extractor *BRA 098/78/2002, TUHH* Germany [*Zetzl et al. 2003; Parisotto et al., 2011*] was used to obtain black cumin extract. Extraction procedure was previously described in literature [*Michielin et al. 2009*]. Extractor had 0.032 m long and 100 mL capacity and the extraction temperature was controlled by a thermostatic bath. The extraction unit also contains valves, flow regulators and manometers for flow control. The extracting conditions were carried out at temperature of 45°C and pressure of 200, 250 and 350 bar; at temperature of 50°C and pressure of 300, 450 and 500 bar, at flow rates of 0.8 (±0.03) kg CO_2/h.

Experimental conditions are presented at the Table 1.

Tab. 1. Experimental conditions

Nr exp	m g	d_{bulk} g/cm^3	P bar	T °C	m_{after} SFE g	m_{extr} g	Errors (Lost)
1	27.09	0.469	200	45	23.60	2.79	20.06%
2	27.06	0.468	250	45	23.00	3.32	18.23%
3	27.33	0.469	350	45	23.32	3.36	16.21%
4	50.07	0.469	300	55	42.77	6.44	11.78%
5	49.80	0.437	450	55	45.80	3.88	3.08%
6	47.90	0.437	500	55	40.50	7.13	3.65%

where: m, g – mass of the raw dry material, d_{bulk}, g/cm^3 – bulk density of seeds, P, bar – pressure, T, °C – temperature, m_{after}, g – mass of material after extraction, m_{extr}, g – the mass of the extract, Errors (Lost) – lost during process

The extractor was filled of 20 g/50 g grounded seeds, with bulk density of 0.437÷0.469 g/cm^3. Relative humidity of the seeds did not exceed 5÷6.8%. Crushed seeds formed the fixed bed for the high-pressure extractions, at controlled conditions of temperature, pressure and solvent flow rate. The extracts obtained during the SFE process were weighed in an analytical balance and the extraction yield was calculated from the total mass. For the global yield determination, many glass flasks were used to collect the extracts, in order to measure the mass extracted in defined time intervals. At each 5÷10 minutes of extraction, the flask was changed by an empty one.

Analytical Methods

Headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry (GC-MS) were performed to analyze volatile fraction of extract.

The SPME fibers (65 µm *Stableflex* DVB/CAR/PDMS) and the holder were obtained from *Supelco Ltd*., (Bellefonte, PA, USA). The fibers were first conditioned according to the manufacturer's instructions. For each extraction, 0.5 g of extract sample was immediately placed in a glass vial with a silicone septum coated with a *Teflon* film. The sample was kept for 15 min in a water bath at 50°C to achieve partition equilibrium between the sample and the air in the vial. Then, the SPME fiber was exposed to the headspace in the vial to absorb the analytes. After 30 min exposure time, the fiber was retracted into the needle and introduced into the GC injector for desorption and analysis of the volatiles. Three SPME analyses were performed in parallel for each oily sample.

The released volatiles were analyzed by Gas Chromatographic analysis GC and GC/MS. The capillary column with FID detector at *Varian 3400* model gas chromatograph were used. The relative composition of each SPME sample was calculated from the GC peak area using correction factors, retention time of volatile components were taken from literature [*Wajs et al., 2008*].

Results and discussion

Volatile contents

Each experiment was performed in triplicate and analyzed with HS-SPME sampling method, followed by GC/MS. The composition of the volatile fraction obtained from the seeds during all runs of experiments contained around 18 different volatile components. Extract volatile oil contents of 5 important compounds are presented on Fig. 1, where the highest amount of thymoquinone, *ρ*-cymene, α-pinene, α-thujene and limonene can be observed.

In previous works, around 9 volatile components of *Nigella* extracts SC-CO_2 for pressure ranges of 100÷250 bar and 14÷37°C were identified using Polish seeds [*Wawrzyniak et al., 2003*]. Using the seeds from India *Venkatachallam et al.* [*2010*] found around 32 volatile components at

Prosimy cytować jako: Inż. Ap. Chem. 2012, 51, 6, 322-323

the SC-CO_2 conditions of 280 bar/50°C and 21 volatile components at the 120 bar/40°C; conventional hydrodistillation gave more than 50% less compounds in the volatile fraction.

That high gap can be explained by climate, ground and cultivation differences of *Nigella* seeds. For the Central European seeds, we obtained the highest value of volatiles.

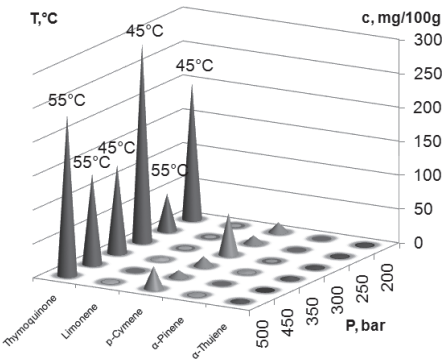

Fig. 1. Extracts volatile oil contents of 5 important substances of black cumin essential oil extracted by batch extraction

SFE kinetics

Besides the confirmation of the high amount of volatiles in the supercritical extract from black cumin seeds, described above, the technical viability of the SFE process is important to the evaluation of economical viability. Therefore, the kinetics study was performed in order to define the region of the extraction where the highest yields were obtained. The global yield (Yield) was calculated by the ratio between extract and feed mass (1),

$$Yield\left(\%, \frac{w}{w}\right) = 100\frac{m_{ext}}{m} \quad (1)$$

where: m_{ext} is the mass of the extract [g], and m – the mass of the raw dry material [g].

The overall extraction curves were obtained at 45°C and at 200, 250, 350; and 55°C and 300, 400 and 500 bar, and solvent flow rate of 8.30 and 13.30 g/min and the results are presented in Fig. 2.

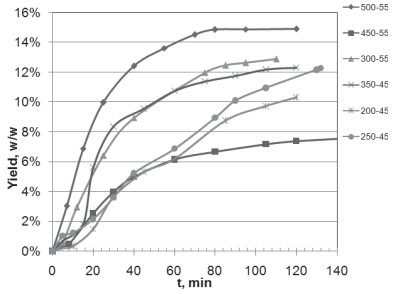

Fig. 2. Accumulated Yield of Extract, Batch SFE Pressure, Temperature SFE curves for black cumin at different conditions of pressure and temperature

We observed the extraction curves, presented a similar behavior, with a constant extraction rate period (CER), followed by a decreasing extraction rate period and ended by a diffusional period, typical for different seeds [*Brunner, 1994; Ferreira et al., 2002*]. Additionally, the increase in flow rate Q_{CO2} (from 0.5 to 0.8 kg/h) enhanced the process yield, probably due to the enlargement in the concentration driving force between solute and solvent phase, as also discussed by several authors [*Wawrzyniak at al., 2003, Ferreira et al., 2002*]. The overall extraction curves, extract mass versus extraction time, were performed for the experimental conditions studied in order to evaluate the process yield and the mass transfer behavior.

In Table 2 are presented determined parameters for the extraction curves.

Tab. 2. Determined parameters for the extraction curves in function of the operational pressure and solvent flow rate evaluated

Nr exp	P/S_{CO2} bar/ (g/min)	t_{CER} min	M_{CER} g/min	Yield, w/w%	ρ_{CO2} g/cm^3	D m^2/s
1	200/ 8.30	90.2	0.033	10.3	0.814	$1.552\cdot10^{-13}$
2	250/ 8.30	75.0	0.039	12.3	0.830	$4.038\cdot10^{-13}$
3	350/ 13.30	67.3	0.046	12.4	0.858	$1.880\cdot10^{-13}$
4	300/ 13.30	89.0	0.038	12.9	0.723	$1.245\cdot10^{-13}$
5	450/ 8.30	64.0	0.092	7.8	0.850	$2.922\cdot10^{-13}$
6	500/ 13.30	73.8	0.096	14.9	0.948	$9.580\cdot10^{-13}$

where: P/S_{CO2} – operation pressure and flow rate of CO_2 [bar/(g/min)]; t_{CER} – time of the CER [min]; M_{CER} – mass extraction rate at CER[g/min]; *Yield* – global yield [w/w%]; ρ_{CO2} – density of of CO_2 [g/cm^3] and D – the diffusivity [m^2/s]

The time (t_{CER}) and mass extraction rate (M_{CER}) of CER (constant extraction rate) period were calculated by the tool for simulation [*BATCHSFE TUHH, 2012*]. The diffusivity D_m was determined by *Simple Single Plate* (SSP) model [*Gaspar et al., 2003*], where $D_m = f(t_{CER}, M_{CER})$. Modified SSP model is neglecting dispersion, were assumed a constant substrate flow with permanent mass transfer to the pore surface; substrate is easy accessible to solvent during CER section; substrate concentration at surface is equivalent to saturation concentration (solubility) [*Gaspar et al., 2003*].

The kinetics study of the SFE of black cumin showed that the operating parameters such as temperature, pressure and solvent flow rate, did affect the mass transfer and the process yield and must be carefully determined combining the quality aspects of the product (extract) and the process efficiency.

Conclusions

This study has clearly brought out the possibilities to obtain higher percentage of valuable volatiles such as thymoquinone and ρ-cymene through high-pressure SC-CO_2 technology. The sustainable conditions of 300 bar and 45°C allowed us to obtain the highest amount of volatile oil yield with maximum volatile content.

REFERENCES

Brunner G.,1994. *Gas extraction: An introduction to fundamentals of supercritical fluids and the application to separation processes.* Steinkopff, Darmstadt & New York

Ferreira S.R.S., Meireles M.A.A., 2002. Modeling the supercritical fluid extraction of black pepper (Pipper nigrum L.) essential oil. *J. Food Engineering*, **54**, 263–269

Fullana M., Trabelsi F., Recasens F., 1999. Use of neural net computing for statistical and kinetic modelling and simulation of supercritical fluid extractors, *Chemical Engineering Science*, **54**, nr 24, 5845–5862. DOI: 10.1016/S0009-2509(99)00179-7

Gaspar F.; Lu T.; Santos B.; Al-Durin B., 2003. Modelling the extraction of essential oils with compressed carbon dioxide, *J. Supercritical Fluids*, 2003, **25**, 247-260. DOI: 10.1016/S0896-8446(02)00149-3

Khan M.A., 1999. Chemical composition and medicinal properties of Nigella Sativa Linn., *InflammoPharmacology*, **7**, nr 1, 15-35. DOI: 10.1007/s10787-999-0023-y

Michielin E., Salvador A., Riehl C., Smania A, Smania E., Ferreira S., 2009. Chemical composition and antibacterial activity of Cordia verbenacea extracts obtained by different methods, *Bioresource Technology*, **100**, 6615-6623, DOI: 10.1016/j.biortech.2009.07.061

Paarakh P., 2010. Nigella Sativa Linn. – A comprehensive review. 2010. *Indian Journal of Natural Products and Resources*, 1, nr 4, 409-429

Parisotto E, Michielin E, Biscaro F, Ferreira S, Filho D, Pedrosa R., 2012. The antitumor activity of extracts from Cordia verbenacea D.C. obtained by supercritical fluid extraction. *J. Supercritical Fluids*; 61, 101-107, DOI: 10.1016/j.supflu.2011.08.016

Venkatachallam Tiruppur S., Pattekhan H, Divakar S., Kadimi S., 2010. Chemical composition of Nigella sativa L. seed extracts obtained by supercritical carbon dioxide. *J. Food Science and Technology,*47, (6), 598-605, DOI: 10.1007/s13197-010-0109-y

Wajs, A., Bonikowski R., Kalemba D. 2008. Composition of essential oil from seeds of Nigella sativa L. cultivated in Poland. *J. Flavour and Fragrance*, 23, 126-132, DOI: 10.1002/ffj.1866

Wawrzyniak P., Kalemba D., Wajs A., 2003. Supercritical carbon dioxide extraction from solid matrix of vegetable origin, *Polish Journal of Chemical Technology*, 5, nr 4, 67-69

Weinhold T., Bresciani L., Tridapalli C., Yunes R., Hense H., Ferreira S., 2008. Polygala cyparissias oleoresin: comparing CO_2 and classical organic solvent extractions, *Chemical Engineering and Processing*, 47, 109–117. DOI: 10.1016/j.cep.2007.08.007

Zetzl C., Brunner G, Meireles M.A.A., 2003. Standardised low-cost batch SFE-units for University education and comparative research. Proceedings of *6th International Symposium on Supercritical Fluids*, Versailles, France, 28-30 April 2003,15-20

BATCHSFE TUHH, 2012 – Tool for simulation (08.2012): http://www.tu-harburg.de/v8/gruppe-prof-smirnova/veroeffentlichungen/batch-sfe.html