Journal of King Saud University – Engineering Sciences xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of King Saud University – Engineering Sciences

journal homepage: www.sciencedirect.com

Technical note

The influence of particle size on supercritical extraction of dog rose (*Rosa canina*) seed oil

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ARTICLE INFO

Article history:
Received 6 February 2018
Accepted 25 April 2018
Available online xxxx

Keywords:
Supercritical CO_2 extraction
Dog rose
Dog rose seed
Residue content
Fatty acid
Linoleic acid

ABSTRACT

The aim of this research was to determine the effect of particle size on dog rose seed oil recovered by the method of Supercritical Fluid Extraction (SFE). Supercritical extraction implemented using dog rose seed particles ($d_1 < 0.27$ mm; $0.27 < d_2 < 0.7$ mm; 0.7 mm $< d_3 < 1.4$ mm) at 30 MPa, 50 °C, 0.228 L/min flow rate of supercritical carbon dioxide and at the 40 °C separation temperature. The experiments were carried out over the period of 120 min. The results showed that maximum oil obtained at smallest particle sizes (maximal absolute yield-7.63 g from 78.2 g seed). The highest volume of the residue in oil was with particles $d_1 < 0.27$ mm. The GC analyses revealed the oil from dog rose seeds was rich of unsaturated fatty acids.

1. Introduction

The process of extraction had an ancient background and basically natural products were extracted for food, pharmacy and perfume industries. The extractions of the natural products include two types of the extraction: mechanical and solvent extractions. The basic principles of the mechanical extraction is pressing and squeezing, solvent extraction carried out using chemical solvents such as hexane, acetone, ethanol etc. The replacement for the conventional method appeared was SFE, which has been revealing huge amount of merits, as well as it is the most marketable green technology. CO_2 as a solvent above critical condition demonstrates itself as gas like and liquid like features. As a supercritical fluid, CO_2 has especially properties such as odorless, environmentally safe, nonflammable, pure, none toxic, recyclable and extraction process can be implemented low temperatures compared to conventional as pointed researchers (Andrea et al., 2013; Chouchi and Barth, 1996; Del Valle and Aguilera, 1989; Lili et al., 2011; Mohammed et al., 2012).

There are numerous impacts of the technological aspects of supercritical fluid extraction on quality and quantity properties of the oil. It can be seen from experiment indexes that more influence of pressure, temperature, fluid flow rate, particle size, filling quantity and period of the extraction on oil recovery rate as well as quality.

It is possible to divide the effects on the supercritical fluid extraction at two groups:

Solid phase factors (*matrix parameters*)

Particle size and shape, porosity, moisture content, sample quantity

Fluid phase properties

Temperature, pressure, density, flow rate which has been studied by various researchers Angelov et al. (2013); Concha et al. (2006); Jian-Zhong et al. (2005); Sairam et al. (2012); Núnez et al. (2017).

Asep et al. (2008) and Soroush et al. (2010) have recently pointed particle size is one of the factors, which have more effect on Supercritical fluid extraction, such as a pressure, temperature and flow rate. Theoretically, reduction of the particle sizes increase extraction effectiveness. This is because diminishing the size of the particles lead to reduce of the diffusion path and greater contact

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.jksues.2018.04.004

Nomenclature

GC	gas chromatography	UFA	unsaturated fatty acids
FAME	Fatty acid methyl ester	P	pressure (Pa)
SFA	saturated fatty acids	T	Temperature (°C)

surface area as a result extraction process accelerates. However, the appearance of the minuscule particles can make the bed and occurs some channels affect consequently, diminish the extraction rate. Above-mentioned concepts were proved by researches, which is experiments have been done on the plant of cocoa liquor, cocoa nib, canola seeds as well as the effects of particle size on the oil content studied. Results revealed that decreasing of the particle size has special impact on volume of the intended substances additionally, triglyceride and fatty acids composition at 35 MPa, 60 °C, with flow rate of carbon dioxide 2 ml/min.

2 Materials and methods

2.1. Preparation for extraction process

Dog rose seeds (*Rosa canina*) were bought from Namangan region of the Uzbekistan. Prior to operation, seeds moisture content and oil content of dog rose seed were determined. The dog rose seed oil content was 10.3% (volume of dog rose seed oil in dog rose seed, determined using Soxhlet method according to (AOAC, 1998)). Moisture content was 5.8%. The dog rose seed was milled (JSP-350, China). Studying of particle sizes passed through a mesh sieve (diameter $d_1 < 0.27$ mm, 0.27 mm < d_2<0.7 mm, 0.7 mm < d_3 < 1.4 mm). Experiments were repeated three times. As a main result demonstrated is arithmetic means of findings repeated for every conditions.

2.2. Supercritical fluid extraction

The system consist conditioner, pumps for CO_2, filters, heaters and extractor tanks with volume 1 L and 5 L, pressure regulator and separators, thermometers and manometers (HA 220-50-06, Nantong Huaan supercritical fluid extraction Co., Limited). The study implemented for the determination of the influence of dog rose seed particle sizes on output parameters of the process at 50 °C, 30 MPa, flow rate of 0.228 L/min using supercritical carbon dioxide and 40 °C separation temperatures. The purity of the carbon dioxide was 99.95% (China). Each experiment performed at the 1 L of volume of the extraction vessel.

Supercritical fluid extraction was carried out above-mentioned apparatus revealed in Fig. 1. Carbon dioxide with density 500 kg/m^3 supplied whole the system from tube **I**. Carbon dioxide leads to filter **II** then cooled by conditioner **III** until 7 °C, liquid phase delivered by pump **IV** until extraction vessel through filters **V** and heater **VI**. Carbon dioxide preheated to the temperature above the intended critical condition. Supercritical fluid interacts with particles of the dog rose seed in the extraction vessel **VII**. Temperature and pressure fixed by controllers for the extraction process. Local temperature of the extraction process was measured inside the vessel by thermometer with accuracy of ±0.01 °C. The pressure of the vessel, which is extraction process occurs measured by manometer with accuracy ±0.01 MPa. The pressure controlled by the valves of 3, 6, 8. There are two non-return valves on the line of the pipe from the CO_2 tube between extraction vessels. Then mixture of the oil and CO_2 from extraction **VII** through the heater **VIII** transported to the separator **IX** with the volume of 2 L. At this point of the system, oil released and CO_2 recycled to the system. Extraction process continued 120 min and measuring intervals were 30 min. The oil gathered into bottle from SFE and measured through balance. After measuring, the bottle containing the extracted oil was transferred into the centrifuge for separation of residue in oil. Yield was calculated by dividing whole amount of

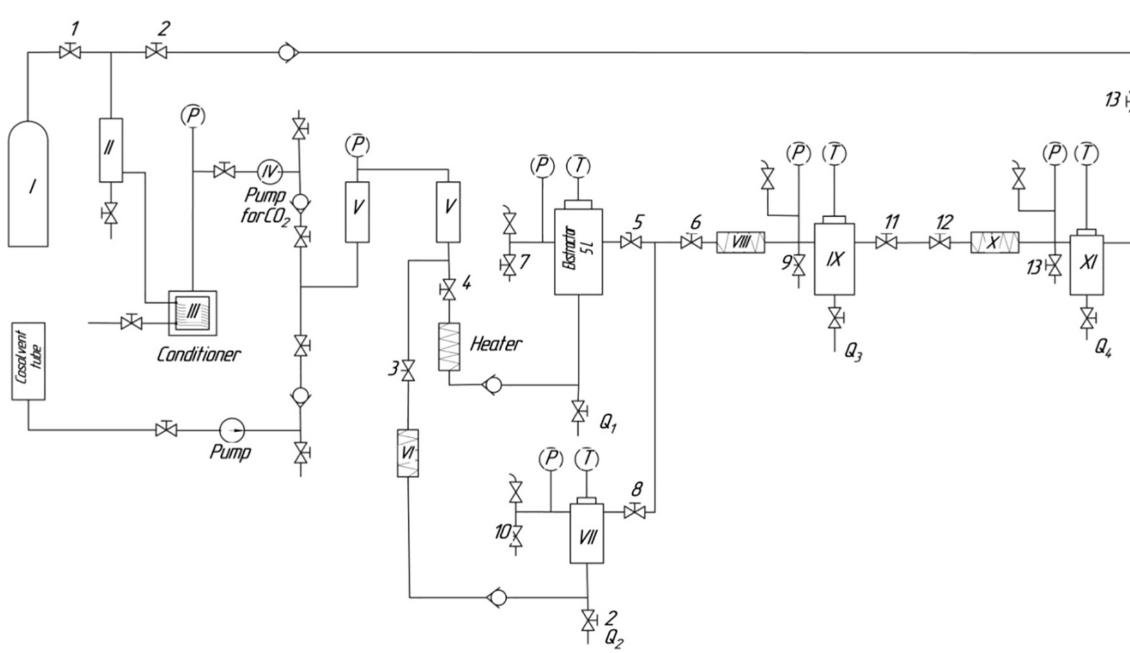

Fig. 1. Flow diagram of the Supercritical fluid extraction.

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oil in the seed with 10.3%. All experiments were carried out in triplicate.

$$percentage = \frac{weight\ of\ oil}{wight\ of\ the\ seed} \times 100\% \quad (1)$$

$$Yield = \frac{percent\ age\ of\ oil}{whole\ oil\ in\ the\ seed} \quad (2)$$

2.3. Chemical analysis

The fatty acids composition was determined according to (NSFACF, 2016) by applying Thermo fisher 1310 gas chromatograph (with FID detector) and chromatographic column TR-WAX (0.25 μm; 30 mm* 0.32 mm). Standard of fatty acid methyl esters ordered from China. Fatty acid methyl esters (FAMEs) were prepared by using 0.2 g samples into a 50 mL round bottom flask with nitrogen protection and 6 mL methanol solution with 0.5 mol/L sodium hydroxide was added. Column temperature was 100 °C for 5 min and then increased to 240 °C at the rate of 4 °C/min. Detector and vaporization temperature were 250 °C and flow rate of the nitrogen was 3.5 ml/min. The injection volume of the sample was 0.5 μL (50:1).

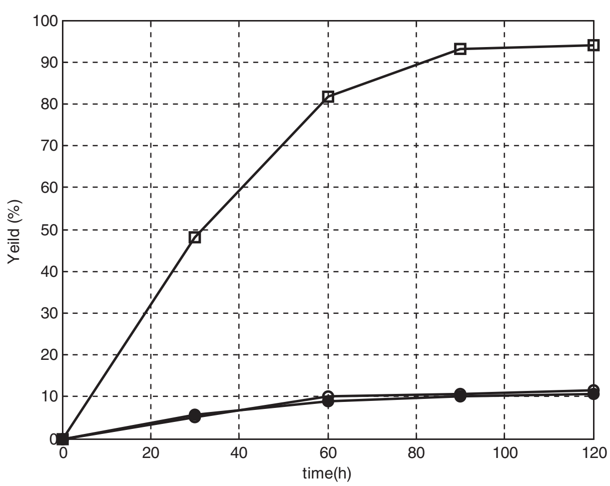

Fig. 2. Effect of the particle sizes on the oil recovery.

3. Results and discussions

Experiments were carried out on different sieved particle sizes of the dog rose seeds (d_1 < 0.27 mm, 0.27 < d_2 < 0.7 mm, 0.7 < d_3 < 1.4 mm) other extraction characteristics were remained the same. (Temperature-50 °C, pressure-30 MPa, separation temperature-40 °C, flow rate-0.228 L/min).

The Fig. 2 shows the effects of different sieved particle sizes on oil yield of the dog rose seed in SFE. From the overall picture of the Supercritical fluid extraction of the dog rose seed curves give information about the similarity of the process theory, whereas the quantity of the oil was different with varying of the sieve fraction. The results show that, the slop of the extraction curves sharply increased until the 90 min with the particle size of the dog rose seed in d_1 compared to d_2 and d_3. At the rest of the time recovering oil volume were almost remains constant among the groups of the sieved particles. Theoretically proven that, reducing of the particle sizes generate enhance of surface area, diminish diffusion path as well as disruptions of the cell walls. Salgın et al. (2016) have recently shown that the yield of the oil recovered in SFE with particles with a size smaller than 500 m were about twice as much as oil removed from bigger sizes of the particle of the dog rose seed. The significant resistance to mass transfer was not noted interior of the pores in the process of SFE with particle sizes of 125 < D_p < 355 μm and 355 < D_p < 500 μm at the operation conditions 30 MPa, 40 °C, 0.75 mL/min. The most part of the oil volume has been extracted about 2 h. Our results showed that the quantity of the oil had not notable difference between the size of particles 0.27 < d_2 < 0.7 mm and 0.7 < d_3 < 1.4 mm. This is may be either impacts of the segregation or the mass transfer limitation remains identically at a sizes of the particles of 0.27 < D_p < 1.4 mm in the process of SFE. Furthermore, the recovered oil with a size of the particles bigger than 0.27 mm were less as compared to the particles with the sizes of d_1 < 0.27 mm. Perhaps the main cause of the large difference of the yield of the oil between d_1 and d_2, d_3 was much more percentage of the tiny particles in d_1 than the others.

A chromatogram of an extract is shown in Fig. 3 and fatty acids composition (area %) of dog rose seed oil extracted at 30 MPa, 50 °C,

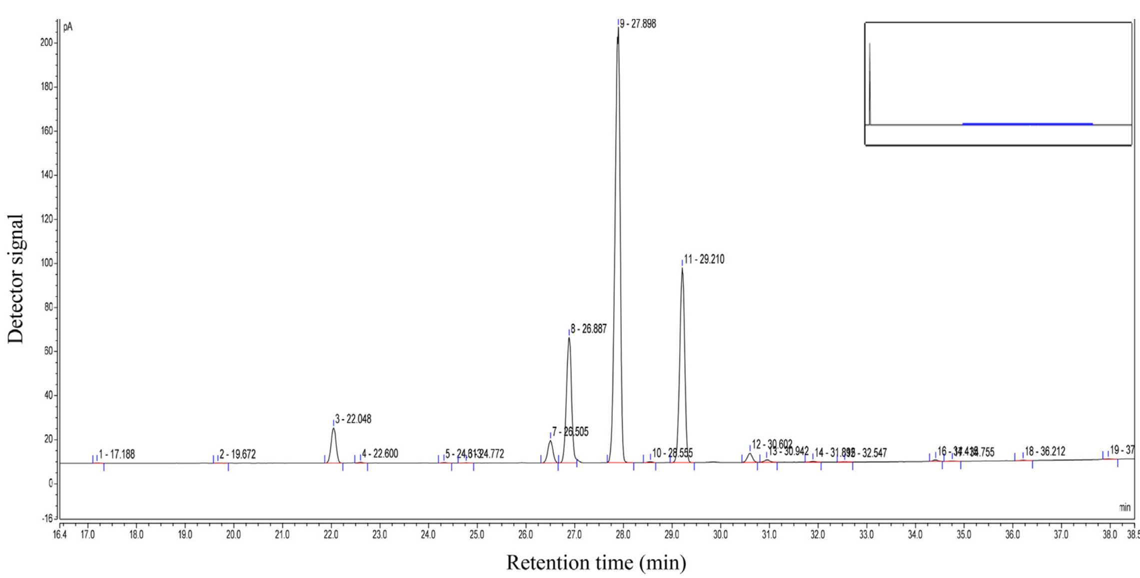

Fig. 3. GC chromatogram of a dog rose seed oil.

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Table 1
Fatty acids composition (area %) of dog rose seed oil.

№	Formula	Retention time (min)	Relative peak area (%)
1	C13:0	17.188	0.03
2	C15:0	19.672	0.01
3	C16:0	22.048	4.08
4	C16:1	22.600	0.12
5	C17:0	24.313	0.06
6	C17:1	24.772	0.04
7	C18:0	26.505	2.67
8	C18:1	26.887	15.18
9	C18:2	27.898	53.08
10	C18:3	28.555	0.09
11	C18:3	29.210	22.68
12	C20:0	30.602	1.10
13	C20:1	30.942	0.30
14	C20:2	31.892	0.10
15	C21:0	32.547	0.03
16	C22:0	34.415	0.16
17	C22:1	34.755	0.07
18	C23:0	36.212	0.05
19	C24:0	37.958	0.12
20	C24:1	38.365	0.02
Total:			**99.99**

flow rate of 0.228 L/min using supercritical carbon dioxide (Table 1).

Özcan (2002) studied in his research impacts of the geographical region on oil from dog rose seed and physical-chemical characters of the seed. The main content of the oil consists linoleic acid with the highest percentage 54.41% which is a bit more than our results. Linolenic and oleic acids represent 18.41%, 18.42% in order. The fundings of Machmudah et al. (2007) demonstrated the dog rose seed oil is composed mainly linoleic acid (C18:2), followed by linolenic (C18:3), palmitic (C16:0) and stearic acid (C18:0) and they concluded extraction conditions effect on fatty acids content. Salgın et al. (2016) have been recently displayed fatty acid compositions of the waste seed oil of the dog rose fruits. The major content of fatty acids of oil obtained by SFE palmitic (2.4%), stearic (2.1%), oleic (20.5%), linoleic (48.3%), linolenic (20.4%), arachidic (1.0 %). Rosa (2018) exhibited the dog rose seed oil properties and fatty acid content (linoleic acid – 51%, linolenic acid – 19% and oleic acid – 20%). Table 1 and Fig. 3 reveal the content of the fatty acids of the oil from dog rose seed as percentages from the total area. The oil content was rich with unsaturated fatty acids, especially linoleic (C 18:2) and linolenic (C18:3), oleic (c18:1) accounted for 53.08% and 22.68%, 15.18% in order. The content of the SFA and UFA was 8.31%, 91.68% respectively. In addition, results show that reducing the size of the sieved particles appears to be more residue content in oil of the dog rose seed. Therefore, the residue content in oil was at the particle sizes of d_1, d_2, and d_3 0.109%, 0.106% and 0.1% in order.

4. Conclusion

The dog rose seeds have been extracted to determine the effect of the particle size. The results revealed that the size of the dog rose seeds influence on the volume of the oil, when the size of the seeds were $d_1 < 0.27$ mm, $0.27 < d_2 < 0.7$ mm, $0.7 < d_3 < 1.4$ mm the percentage of the oil were recovered 94.1%, 11.46% and 10.66% in order. According to the results of study highest oil volume obtained is with optimum size of $d_1 < 0.27$ mm. The highest volume of the residue in oil was with particles $d_1 < 0.27$ mm. The main content of the oil from dog rose seeds were unsaturated fatty acids such as linoleic (C 18:2), linolenic (C18:3) and oleic (c18:1).

Acknowledgment

The authors acknowledge the supports for laboratory facilities of Shandong Academy of Sciences and Tashkent chemical technological institute.

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