

Modelling of Hyssop-Supercritical Carbon Dioxide Extraction System

Sabina Begić¹, Vladan Mičić², Zoran Petrović³, Pero Dugić⁴

Assistant Professor, Department of Chemical Engineering and Technology, Faculty of Technology, Tuzla, Bosnia and Herzegovina¹

Associate Professor, Department of Chemical Engineering, Faculty of Technology, Zvornik, Bosnia and Herzegovina²

Assistant Professor, Department of Chemical Engineering, Faculty of Technology, Zvornik, Bosnia and Herzegovina³

Associate Professor, Oil Refinery, Modriča, Bosnia and Herzegovina⁴

ABSTRACT: The Hyssop officinalis L. was extracted using supercritical carbon – dioxide (SFE – CO₂) as extractant. Extraction was carried out in the two steps: the first one being carried out at 100 bar and 40°C in time 4 h for the mean particle size 0.49 mm (extract A), and the second was the extraction of the hyssop sample at same conditions (pressure, temperature and time) for the mean particle size 0.13 mm (extract B).

The supercritical fluid extraction (SFE) with carbon dioxide was carried out using a laboratory scale high pressure extraction plant - HPEP (Nova Swiss, Effretikon, Switzerland). Separator conditions were 15 bar and 25 °C.

Extraction kinetics of the system hyssop – SFE – CO₂ was investigation. Mathematical modeling using Modified Reverchon - Sesti Osseo equation has been performed on Hyssop officinalis L. With modified equation fitted results was well.

KEYWORDS: Hyssop, Supercritical extraction, Modelling, Carbon – dioxide.

I. INTRODUCTION

With increasing public interest in herbal medicine and natural products, the conventional methods such as hydro-distillation and solvent extraction were found unsatisfactory. Conventionally, the essential oils of the aromatic herbs have been isolated using hydro-distillation and/or solvent extraction. However, low yield, loss of volatile compounds, long extraction times, toxic solvent residue, degradation of unsaturated compounds and production of undesirable off - flavours (due to heat) are involved in using such technique. To improve efficiency and selectivity of the extraction, alternative extraction techniques as supercritical extraction started to be developed.

Supercritical extraction is not widely used yet, but as new technologies are coming there are more and more view points that could justify it, as high purity, residual solvent content and environment protection [1], [2], [3].

As an alternative approach, supercritical fluid extraction (SFE) has received increasing attention in the extraction of essential oils. This is due to fact that the supercritical fluids can provide improved mass-transfer rates and the operation can easily be manipulated by changing the pressure and/or temperature of the system. Also by optimizing these parameters, certain compounds can be selectively isolated from the drug. Carbon dioxide in its supercritical state has been used in many SFE applications [4], [5], [6].

Carbon dioxide is the most commonly used supercritical fluid, due primarily to its low critical parameters (31.1°C, 73.8 bar), low cost and non-toxicity. Supercritical carbon dioxide (SCCO₂) has found applications in the extraction of flavors and fragrances from their natural sources and as a result many studies have been published using this environmentally friendly extraction method. The extraction of coriander seed [7], chamomile [8], Thymbra spicata [9] and Carom copticum [10] are just a few of numerous studies reported in the literature using SCCO₂ for the extraction of spices and medicinal herbs. Hyssop (Hyssopus officinalis), which is one of the most important pharmaceutical herbs, is extensively cultivated in central and south European counties such as Russia, Spain, France and Italy [11].

Hyssop is used as a food flavour and also in sauce formulations. Hyssop oil possesses antifungal and anti-bacterial properties which are essential in such industries as canning, beverages and cosmetics. Food industry can always benefit

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 6, June 2014

from the new approaches leading to more hygienic ingredients such as food flavours. The essential oil of Hyssop from different origins has been reported using the traditional methods of extraction [12], [13], [14], [15], [16]. Further more, solvent extraction as well as other methods including SFE with single operational conditions, have been employed for determination of chemical composition of the essential oils of Hyssop [17], [18].

The objectives of the present work were to investigate the effect of several SFE parameters (pressure, temperature, mean particle size) in the SCCO₂ extraction of Bosnia hyssop. For the purposes of mathematical modeling there are numerous models dealing with SFE of essential oils and related products from plant material. Reverchon [19], classified existing models as: 1. Empirical, based on Langmuir –like empirical equation, 2. Models originated from heat transfer analogy, where SFE is treated as heat transfer phenomena, and 3. Models based on differential mass balance, where mass balance along a section of the extractor has been widely used to describe the behaviour of fixed beds during solid/liquid operations like adsorption/desorption, reaction, and extraction.

Hortacsu [2], classified available models as models, where extraction is defined as chemical reaction, and models where extraction is considered as physical phenomenon. The other approaches are Differential Mass Balance Models (i.e. Shrinking Core Model, Desorption –Dissolution –Diffusion Model) and other representations (like Models with Cellular Structure Representation, and Empirical Desorption Models).

II. EXPERIMENTAL

Plant materials

For this experiments Hyssop. from Novi Grad, west part of Republica Srpska, state Bosnia and Herzegovina gathered 2007 was used. All extractions were performed using the Hyssop of the grinding degree d₁ and d₂ (mean particle radius d₁ = 0.49 mm and d₂ = 0.43 mm).

Chemicals

Commercial carbon dioxide (Tehnogas, Novi Sad, Serbia) were used. All other chemicals were of analytical reagent grade.

Supercritical fluid extraction

SFE by CO₂ was carried out on a laboratory – scale high pressure extraction plant (HPEP, NOVA – Swiss, Effretikon, Switzerland). The main parts and characteristics (manufacturer specification) of the plant were as follows: a diaphragm – type compressor (up to 1000 bar), extractor with an internal volume of 200 mL (P_{max} = 250bar), and maximum CO₂ mass flow rate of approximately 5.7 kg/h.

The mass of hyssop in extractor was 60g at the investigated value of pressure (100 bar) and temperature (40°C), the CO₂ flow rate was 97.72 dm³/h. Separator conditions were 15 bar and 25°C.

III. EXPERIMENTAL RESULTS

For modeling of investigated hyssop – supercritical carbon dioxide extraction system in this paper, we used modified Reverchon - Sesti Osseo equation (1994).

$$Y = 100[1 - \exp(-at + b)] \tag{1}$$

where Y is the normalized extraction yield (%); t is the extraction time, a is a constant; b is a correction term

$$Y = \frac{Y_{ext}}{Y_{max}} \cdot 100$$

where:

Y_{ext} is the extraction yield,

Y_{max} is the maximal extraction yield.

This modification was introduced by A. Tolic. Now, we introduce Z defined as

$$Z = \ln\left(1 - \frac{Y}{100}\right) \tag{2}$$

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 6, June 2014

Standard Error of Regression ($S_{Y,X}$) of Model equation for supercritical extraction of Hyssop was calculated with term

$$S_{Y,X} = \sqrt{\frac{\sum(Y_E - Y_i)^2}{n}}$$

where:

Y_E is experimental value,

Y_i is the calculated value,

n is the number of experimental points.

In table 1 are given the experimental and calculated values of Y and values of Z for different particle size. By using Z in the function of time, plots were constructed (Fig. 2), and then parameters a, b are calculated (table 2).

Table 1. Experimental and calculated value of extract yield (Y) and value Z in function of mean particle diameter size of drug

Time (h)	d (mm)					
	d_1			D_2		
	Y	$Y_{ra\check{c}}$	Z	Y	$Y_{ra\check{c}}$	Z
0.5	19.67	10.60	-0.219	24.02	0.0	-0.275
1	47.58	46.74	-0.646	38.65	40.31	-0.489
1.5	72.29	68.27	-1.283	57.19	64.39	-0.848
2	77.03	81.10	-1.471	72.57	78.75	-1.293
2.5	87.31	88.74	-2.064	87.61	87.32	-2.088
3	89.53	93.29	-2.257	91.94	92.44	-2.518
3.5	97.58	96.00	-3.721	96.42	95.49	-3.330
4	100	97.62	-	100	97.31	-
	$y_{max} = 1.032$			$y_{max} = 1.203$		
	$S_{y,x} = 4.215$			$S_{y,x} = 9.207$		

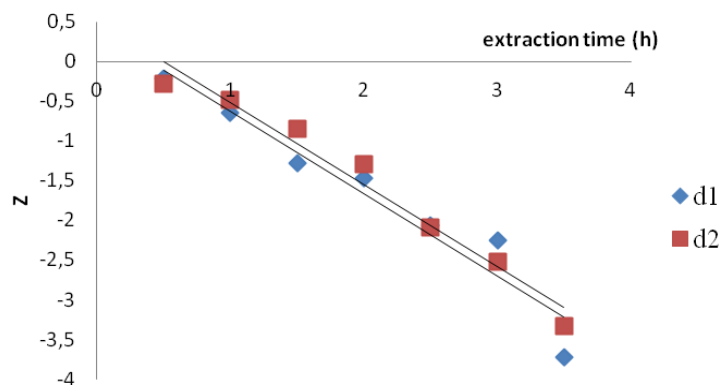


Fig.1. Plot of Z vs. extraction time

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 6, June 2014

Table 2. Parameters a and b in Equation (1) for given grinding degree

d (mm)	A	B	r
d ₁ = 0.49	-1.036	0.406	0.966
d ₂ = 0.13	-1.033	0.517	0.984

Further, calculated values for parameters a and b are substitute in Equation 1, and this equation was used for obtaining normalized total extract yield of Hyssop, at supercritical extraction by carbon dioxide (table 3).

Table 3. Modified equation for calculating normalized yield of total extract for different grinding degree of drug

d (mm)	Modified Reverchon - Sesti Osseo equation
d ₁	Y = 100[1-exp(-1.036t + 0.406)]
d ₂	Y = 100[1-exp(-1.033t + 0.517)]

IV. CONCLUSION

Mathematical modeling using Modified Reverchon - Sesti Osseo equation has been performed for Hyssop. The calculated values of standard error of regression show that the modified equation in general has good fit for normalized yield of total extract. Also high value of correlation coefficient (r) shows that the given equation can be used for modeling hyssop –supercritical carbon dioxide extraction system.

REFERENCES

- [1] E. Reverchon, "Supercritical fluid extraction and fractionation of essential oil and related products", in Journal of Supercritical Fluids, vol. 10, No.1, pp. 1-37, 1997.
- [2] O. Hortacsu, "Modeling of natural materials extraction" in E. Kiran at all (Eds.), Supercritical Fluids: Fundamentals and Application, Dordrecht, Netherlands: Kluwer Academic Publishers, pp. 499-516, 2000.
- [3] M. M. Esquivel, M. G. Bernardo-Gil, M. B. King, "Mathematical models for supercritical extraction of olive husk oil", in Journal of Supercritical Fluids, vol. 16, No. 1, pp. 43-58, 1999.
- [4] E. Cassel, C. D. Frizzo, R. Vanderlinde, L. Atti-Serafini, D. Lorenzo, E. Dellacassa, "Extraction of Baccharis oil by supercritical CO₂" in Industrial and Engineering Chemistry Research, vol. 39, No.12, pp. 4803-4805, 2000.
- [5] F. Le Floch, M. T. Tena, A. Rios, M. Valcarcel, "Supercritical fluid extraction of phenol compounds from olive leaves", in Talanta International Journal of Pure and Applicable Analytical Chemistry, vol. 46, No.5, pp. 1123-1300, 1998.
- [6] M. T. Morales, A. J. Berry, P. S. McIntyre, R. Aparicio, „Tentative analysis of virgin olive oil aroma by supercritical fluid extraction-high resolution gas chromatography-mass spectrometry" in Journal of Chromatography A, vol. 819, No.1-2, pp. 267-275, 1998.
- [7] V. Illes, H. G. Daood, S. Perkencki, L. Szokonya, M. Then, "Extraction of coriander seed oil by CO₂ and propane at super- and subcritical conditions", Journal of Supercritical Fluids, vol. 17, No. 2, pp. 177-186, 2000.
- [8] N. P. Povh, M. O. M. Marques, M. A. A. Meireles, "Supercritical CO₂ extraction of essential oil and oleoresin from Chamomile (Chamomilla recutita L. Rauschert)", Journal of Supercritical Fluids, vol. 21, No. 3, pp. 245-256, 2001.
- [9] S. Sonsuzer, S. Sahin, L. Yilmaz, "Optimization of supercritical CO₂ extraction of Thymbra spicata oil", Journal of Supercritical Fluids, vol. 30, No.2, pp. 189-199, 2004.
- [10] M. Khajeh, Y. Yamini, F. Sefidkon, N. Bahramifar, "Comparison of essential oil of Carom Copticum obtained by supercritical carbondioxide extraction and hydro-distillation methods" in Food Chemistry Journal, vol. 86, No. 4, pp. 587-591, 2004.
- [11] R. Omidbaigi, "Production and processing of medical plants", 3th ed., Astan Quds Razavi Publications, Behnashr Co., Mashad, Iran, 2000.
- [12] S. N. Garg, A. A. Naqvi, A. Singh, G. Ram, S. Kumar, "Composition of essential oil from an annual crop Hyssopus officinalis grown in Indian plains", in Flavour and Fragrance Journal, vol. 14, No.3, pp. 170-172, 1999.
- [13] M. S. Gorunovic, P. M. Bogavac, J. C. Chalchat, J. L. Chabard, "Essential oil of Hyssopus officinalis L., Lamiaceae of Montenegro origin", in Journal of Essential Oil Research, vol. 7, No.1, pp. 39-43, 1995.
- [14] M. Jankovski, T. Landa, "Genus Hyssopus L. – recent knowledge" in Horticultural Science Journal, vol. 29, No. 3, pp. 119-123, 2002.
- [15] G. Schulz, E. Stahl-Biskup, „Essential oils and glycosidic bound volatiles from leaves, stems, flowers and roots of Hyssopus officinalis L. (lamiaceae)", in Flavour and Fragrance Journal, vol. 6, No. 1, pp. 69-73, 1991.
- [16] E. T. Tsankova, A. N. Kontaktchiev, E. M Genova, "Chemical composition of the essential oils of two Hyssopus officinalis taxa", in Journal of Essential Oil Research, Vol. 5, No.6, pp. 609-611, 1993.
- [17] T. Kerrola, B. Galambossi, H. Kallio, „Volatile components and odor intensity of four phenotypes of Hyssop (Hyssopus officinalis L.)" in Journal of Agricultural Food Chemistry, vol. 42, No.3, pp. 776-781, 1994.
- [18] V. Mitić, S. Đorđević, "Essential oil composition of Hyssopus Officinalis L. Cultivated in Serbia", in Facta Universitatis, vol. 2, No.2, pp. 105-108, 2000.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 6, June 2014

- [19] E. Reverchon, and L. Sesti Osseo, "Modeling the supercritical extraction of Basil oil", Proceedings of the 3rd International Symposium on Supercritical Fluids, vol. 2, pp. 189-196, 1994.
- [20] B. Pekić, A. Tolić, Z. Lepojević, Z. Zeković, "Application of our modification of the Reverchon-Sesti Osseo equation to the supercritical extraction of camomile flower by carbon dioxide", in Book of Abstracts - 1st International Conference of Chemical Societies of the South-East European Countries, Halkidiki, Greece, vol 1, pp. 1654, 1998.