EXTRACTION OF VEGETABLE OILS FROM GROUND SEEDS BY PERCOLATION TECHNIQUES

Mălina AVRAM[1], Anicuța STOICA[2], Tănase DOBRE[3], Marta STROESCU[4]

An experimental bench-scale plant based on percolating procedure was built-up, in order to investigate the solvent extraction for oil separation from ground rapeseed, soybean and sunflower. n-Heptane and hexane have been used as extraction solvents. The extraction time, the solvent to ground seeds mass ratio and the ground particle size were considered as process factors. A thermal regime near to solvent boiling point was assumed. A detailed description of the extraction yield dynamics and its correlation with the operating conditions are given by the experimental results, obtained for different values of process factors.

Keywords: oil extraction, ground seeds, percolation procedure, shrinking core model

1. Introduction

The worldwide oil seed production will face an increasing demand in the next thirty years due to the combination of factors, including a higher consumption for edible oil, the development of the biofuel industry, and the needs for green chemistry. Nowadays, the annual worldwide oil production is close to 135 Mt with palm, soybean and rapeseed oils representing 31%, 24% and 15% of the total production respectively [1]. Vegetable oils represents a particular importance as raw materials for industries like food (for their nutritional value), energetic (through their conversion in renewable biofuels), or chemical (detergents or materials industry, film-forming substances like varnishes, paints, and so on). Now the major interest is for the energetic application regarding the development of biofuels from various materials. In Romania, the main oil crops used are: soybean, sunflower, line, rape, mustard and castor [2, 3]. Even if the oilseed industry is a consolidated one, there is still the possibility to improve solvent extraction using new processing conditions and new apparatus [4]. For example, a twin-screw extruder was already proposed as a machine to conduct a

[1] PhD student, INCDCP-ICECHIM, Chemical Engineering Department, University POLITEHNICA of Bucharest, Romania, e-mail: malinaavram@yahoo.com
[2] Prof., Chemical Engineering Department, University POLITEHNICA of Bucharest, Romania
[3] Prof., Chemical Engineering Department, University POLITEHNICA of Bucharest, Romania, corresponding author: e-mail: tghdobre@gmail.com
[4] Prof., Chemical Engineering Department, University POLITEHNICA of Bucharest, Romania

thermo-mechanical pressing and a solvent extraction of sunflower oil in a single step and in a continuous mode [5]. The processing conditions improvement is not the only goals of those who study oilseed extraction, but also the development of new models able to explain the observed phenomena during extraction. From the earlier models reported during 1950's one could observe a constant evolution of the proposed model in order to explain the comportment during extraction of the vegetable materials. The most widely accepted model considers two main mechanisms which occur during extraction a washing process of the oil on the grain surface and a diffusion process from the broken and intact cells that remain after pre-extraction treatments [4-9].

In the present work, an experimental bench-scale plant was built-up in order to investigate the oil separation from ground seeds (especially ground rapeseed) by using n-heptane and hexane as extraction solvents. Different extraction times, different ratio solvent to ground rapeseed and different particle size has been considered for process investigation. Beside the different fatty acid content, rapeseed, soybean and sunflower oil are characterized mainly by their carotenoids and vitamin E content [10]. The chemical composition of oleaginous materials is different depending on variety and climatic conditions. At present time the rapeseed oil are especially used for manufacturing of biodiesel. For other technical purposes they have multiple uses such as lamp oil, as a component of mineral oils and in manufacturing of lubricating greases. The rapeseed meal contains thioglycoside, which through enzymatic hydrolysis release irritating and toxic compounds [11].

All extraction processes have three common goals: i) to obtain an undamaged oil; ii) getting oils with a high yield as possible and economically efficient; iii) getting high quality oil residue in order to obtain a high economic value of the extraction process. Rapeseed oils are extracted by several methods. These methods include mechanical, solvent, enzymes and high pressure CO_2 extraction. Solvent extraction is the most efficient method of removing the oil from the seed. It may take place either in batch or continuous process. The solvent extraction most commonly used today is percolation with a countercurrent flow using hexane as solvent [5].

The rate of extraction depends on the thickness and area of solid phase, temperature, solvent and moisture content [12]. Depending on the variety and growing conditions, the chemical composition of rapeseed [13, 14], is characterized by a content of 33-49% lipids, 19-20% crude proteins and 17-18% non extractable compounds.

The goal of this paper is to obtain experimental data for fixed bed extraction of rapeseed, soybean and sunflower oil using hexane and n-heptane as solvent in order to prove that the shrinking core model could be used for process modelling.

2. Experimental methodology

For extraction, two installations were used, one of them being a personal design. The first was the Soxhlet extractor and the second is a column type extraction installation, presented in Fig. 1a. The Soxhlet extractor was used in order to establish the maximum amount of oil in the seeds, the optimum extraction time, the optimal amount of solvent used for extraction and the optimal particle size of the ground material. In the experimental bench-scale plant presented in Fig. 1a, the extraction is based on a fixed bed percolation method. As it can be seen, the oil extraction plant is composed of a pot (reboiler), an extraction column, insulated tube for vapour transport and condenser. In order to maintain optimal thermal parameters and to prevent heat exchange with the surrounding environment the extraction column is insulated with asbestos material. Inside the column a perforated plate support the ground seeds and allowed the circulation of solvent vapours at the bottom of fixed bed. The condenser is cooled with water. Inside of the device a steady state temperature distribution is rapidly installed after boiling starts in the reboiler. At the end of the extraction the seed cake is weighted after drying and the pot content is weighted and then distilled in order to separate the oil from the solvent. The recovered solvent was reused in new experiments. In order to establish the oil composition, gas chromatographic analysis was performed. To characterize the seed oil extracts by gas chromatography (GC), fatty acid methyl esters were obtained by transesterification using 14% boron tri-fluoride in methanol as catalyst.

Fatty acid analysis was performed on a Perkin-Elmer Clarus 500 GC equipped with an FID detector. The type of the column was: SGE BPX70: L = 50 m; ID = 0.22 mm; Film φ = 0.25 μm (column for fatty acid esters). An internal standard C17 (methyl heptadecanoic) could be used to determine the concentration of fatty acid esters, but in the case of rapeseed oil the analysis was done without internal standard, and was measured only a relative distribution of esters based on retention times (T_R) previously determined for each compound from standards. Standards which were used for each fatty acid esters with concentration of 99.5% were purchased from Fluka company.

Fatty acid methyl esters were prepared according to AOCS method from 1997 as follows: 200 mg of sample were weighed in a covered glass, over which were added 2 mL heptane and 0.1 mL methanolic solution 2N of potassium hydroxide. The sample was centrifuged for 30 sec. Then, from the upper layer, 2 drops were taken and were diluted in 2 mL heptane and it was injected into GC. The GC analysis was used to determine the fatty acid composition by injection of 1 μL of sample prepared as before. The carrier gas
was hydrogen (20 mL/min) using a split ratio of 1:100. The detector and injector were set at the same temperature, 250°C. The oven temperature was intially

120°C and then was raised to 220°C at 4°C/min, and finally mentained at 220°C for 10 minutes.

The oil content of each sample collected during an experiment is obtained by mean of a refractometric analysis. This content is used for computation of the momentary state of oil extraction yield. For each experiment the time tendency of extraction yield should be directed to final yield resulting after separation of the oil from the solvent.

According to shrinking core model, Fig. 1b, the oil extraction consists [15, 16] of three major steps: i) solubilisation of solute molecules from the liquid-solid interface in the solvent; ii) diffusion of the solute molecules from the solid-liquid interface through the surface layer to the outer boundary of the surface layer; iii) diffusion of the solute molecules from the outer boundary of the surface layer to bulk liquid phase. The shrinking core model parameters are represented by oil saturation concentration in solvent (C_S), effective diffusion coefficient for oil in leached zone of particle (D_{eff}) and oil diffusion coefficient in the bulk liquid (solvent). Solvent flow velocity (w) and axial dispersion coefficient (D_l) are the parameters of model characterising the fixed bed oil transport.

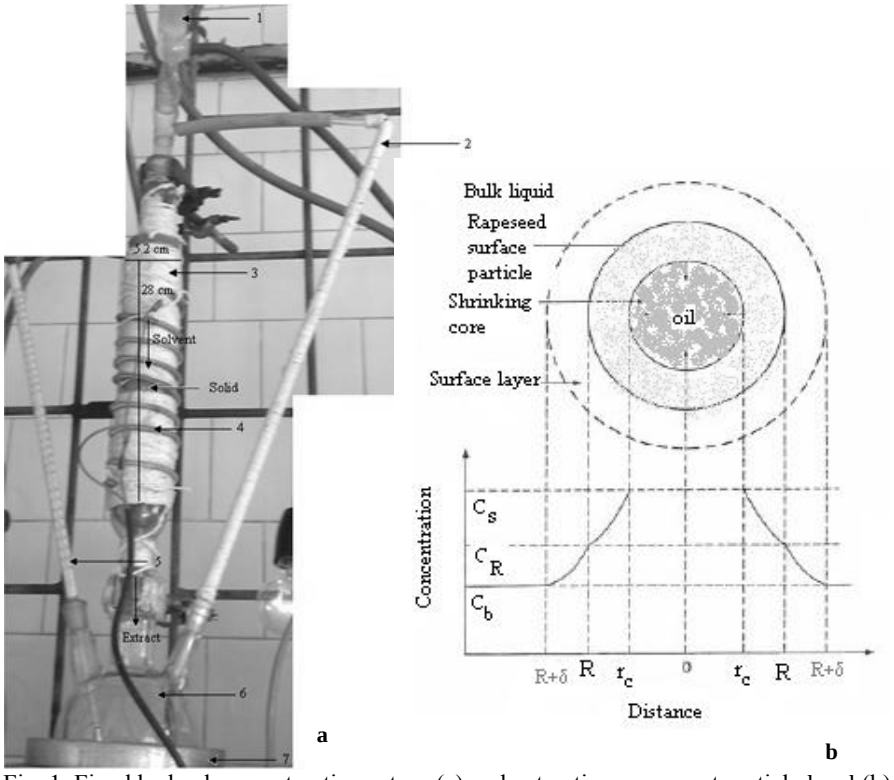

Fig. 1. Fixed bed column extraction set-up (a) and extraction process at particle level (b).

1- condenser; 2- vapours tube (insulated with asbestos thread); 3- extraction column (insulated column with asbestos thread) ; 4- electric resistance heaters for column temperature control ; 5- thermometer; 6- round-bottom flask for solvent; 7- electrical heating mantle.

For a series of experiments with the same flow velocity in the bed, the shrinking core extraction model is indicated by the followings: i) the curves of the extraction yield versus time are similar, all having the shape characterizing a processes with diffusive control; ii) the curves of the extraction yield versus time clearly depend on particle dimension; iii) there are no dependency of these curves path on solvent type when the oil and the tested solvent are completely miscible.

3. Results and discussions

The fatty acids extracted with n-heptane from rapeseed oil, identified by GC analysis after transesterification, consists mainly in oleic (C18:1n9, 61%) and linoleic acid (C18:2n6, 19.8%), but beside them there is a high content of octadecatrienic acid (C18:3n4, 7.2%), palmitic acid (C16, 4.8%), arachidonic acid (C20, 1.2%), linolenic acid (C18:3n3, 0.5%) and others in smaller quantities, as it can be seen from the chromatogram presented in Fig. 2.

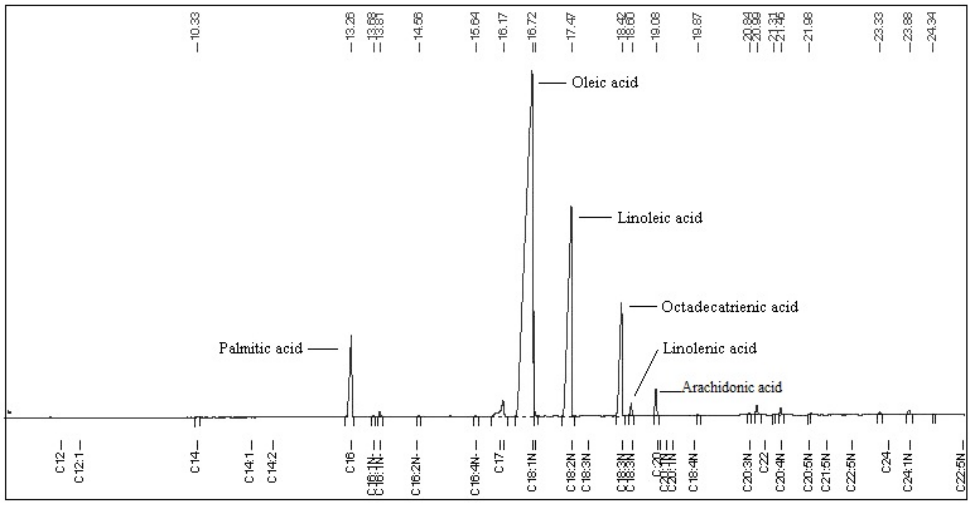

Fig. 2. Composition in fatty acids of rapeseed oil extract obtained by GC

The effect of the particle size of the ground seeds and the solvent type on dynamics of extraction yield is presented in Fig. 3. As it can be seen the amount of extracted oil is dependent on the granulation of the oleaginous material, undergone of extraction. On the other hand no major differences in extraction yield dynamics could be observed between the two solvents used, probably due to

the high solubility of the oil in both solvents. One can see from Fig. 3 that all curves has a similar shape which are likewise to those characterizing an internal diffusion controlling extraction process. With other words, the Fig. 3 shows that the shrinking core model can be applied for designing the rapeseed oil solvent extraction.

The time evolution of the extraction yield from ground soybean using hexane as solvent, for three different particle size is presented in Fig. 4. From Fig. 4 one can see a similar evolution of extraction yield with those obtained for rapeseeds.

If the oil saturation concentration can be accepted to have the same value in both cases then, with respect to shrinking core model, it means that for both materials the oil effective diffusion coefficient ($D_e = \varepsilon D_m / \zeta$) has the same order of magnitude. The use of the same solvent (hexane) in both cases and the consideration that the two oil extracts (from rapeseed and soybean) has the same composition strongly sustain the above hypothesis. Since the molecular diffusion coefficient is determined by the oil-solvent system, it can be assumed that for the both ground oleaginous materials, the ratio between surface porosity and pore tortuosity (ε / ζ) presents the same value.

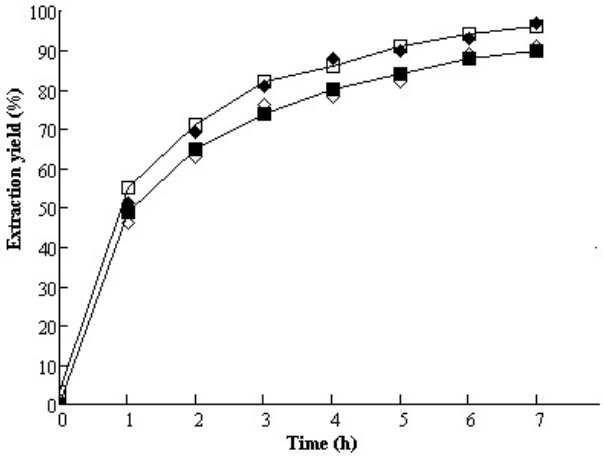

Fig. 3. Effect of particle size and solvent type on the extraction yield dynamics of rapeseed oil (bed height- 10 cm; solvent flowrate– 10 mL/min; □, ♦- hexan respectively n-heptane as solvent and 0.2 mm particle size; ■, ◊- hexan respectively n-heptane as solvent and 0.4 mm particle size; temperature– 69°C for hexan, 98°C for n-heptane)

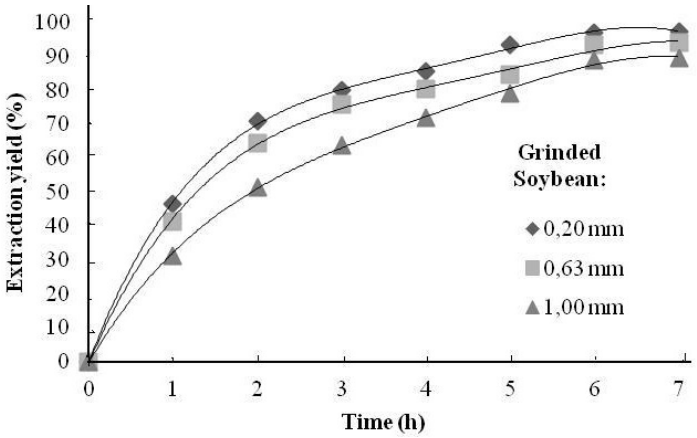

Fig. 4. Effect of particle size on the oil extraction yield from soybean (bed height- 10 cm; solvent flowrate– 10 mL/min; temperature– 69°C)

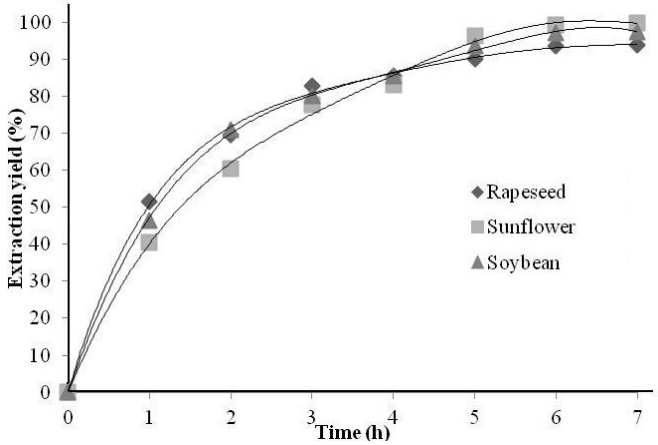

Fig. 5. The dynamics of extraction yield for rapeseed, sunflower and soybean oil (bed height- 10 cm, solvent flow rate– 10 mL/min, solvent- n-heptane, temperature– 97°C, particle size- 0.2 mm)

The time evolution of the extraction yield from sunflower seeds, rapeseeds and soybean, performed in the same conditions presents no major differences, as it can be seen from Fig. 5.

The high solubility of oil from the tested ground seeds in the used solvents and the assumption that the process proceed after the shrinking core model (with internal particle resistance) leads to the conclusion that the oleaginous solid phase type and solid/liquid contacting procedure do not influence in an important way the dynamic of the extraction yield. Data obtained for rapeseed oil extraction yield dynamics in fixed bed percolation and Soxhlet extraction, depicted in Fig. 6, sustain these hypotheses.

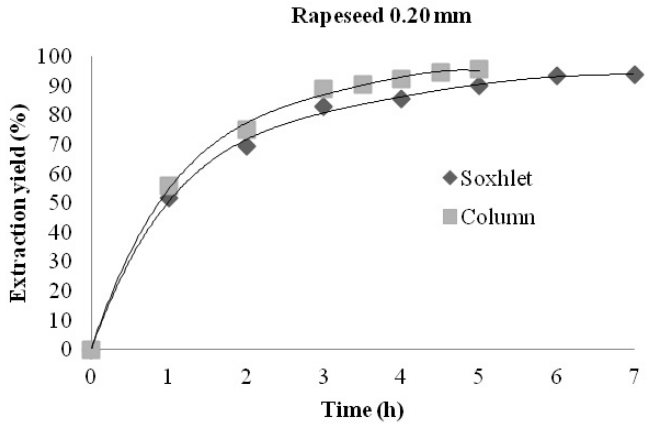

Fig. 6. The dynamics of extraction yield versus time for ground rapeseed fixed bed percolation and Soxhlet extraction (fixed bed height- 10 cm, fixed bed solvent flow rate– 10 mL/min, Soxhlet solvent flow rate– 8 mL/min, Soxhlet bed height- 5 cm, solvent- n-heptane, fixed bed operating temperature– 97°C, Soxhlet operating temperature- 40°C, particle size- 0.2 mm)

Table 1 present the experimental data obtained for rapeseed oil extraction using hexane and n-heptane as solvent. The experimental extraction yield was calculated knowing the oil content of ground rapeseed (45%). For a good extraction yield, as it can be seen from table 1, a solid-liquid mass ratio of 1:2 and no more than 4 hours and 30 minutes as extraction time are needed.

Table 1

State of extraction yield for various working condition at processing of 0.2 mm ground rapeseed particles

No	Incoming raw materials		Outgoing products				Extraction temp.		Time	Exp. procedure
	Sample mass	Solvent	Oil		Recov. solvent	Dry cake	Reboiler solvent	Column solvent		
	g	g	g	$\eta_{extr.}$ %	g	g	°C		min.	
1	200	264 n-C_6H_{14}	85	**94.4**	188.1	115	73	62.5	270	P
2	200	264 n-C_6H_{14}	86	**95.5**	240.9	114	69.5	69	270	P
3	200	264 n-C_6H_{14}	83	**92.2**	198	117	69.5	69	240	P
4	200	264 n-C_6H_{14}	86	**95.5**	224.4	114	69	69	300	P
5	200	396 n-C_6H_{14}	89	**96.9**	341.8	111	69.5	69	300	P
6	200	396 n-C_6H_{14}	87	**96.7**	351.7	113	69.5	69	300	P
7	200	396 n-C_6H_{14}	86.5	**96.1**	368.2	113.5	69	69	300	P

8	200	408 n-C_7H_{16}	89.5	**97.4**	286.2	110.5	99	98	270	P
9	30	66 n-C_6H_{14}	13.5	**99.9**	33	16.5	68	-	360	S
10	30	68 n-C_7H_{16}	13	**98.3**	27.2	17	98	-	360	S
11	200	408 n-C_7H_{14}	90	**98.1**	306	110	99	98	270	P
12	200	408 n-C_7H_{16}	89	**98.8**	319.6	111	99	98	270	P
13	150	306 n-C_7H_{16}	67	**97.2**	260	83	99	98	200	P
14	100	204 n-C_7H_{16}	44.7	**91.3**	183.6	55.3	99	98	135	P
P- Fixed bed percolation, S- Soxhlet extraction										

4. Conclusions

The oil extraction from oleaginous materials using the percolation process was investigated. As raw materials rapeseed, soybean and sunflower ground seeds and hexane and n-heptane as solvent were used. The extraction process in Soxhlet extractor and in an original experimental set-up with a column type fixed bed extractor respectively was performed. The solvent type, particle size solvent-ground seeds mass ratio and oleaginous material type were select for process factors. Extraction yield was chosen for monitoring the extraction process evolution. The time evolution curves of the extraction yield indicate that they are of similar shape and show no dependency on the oleaginous material tested (ground rapeseed, soybean and sunflower seed) and on solvent type, but it clearly depends on particle size and moderate on the operating temperature. Also, all the curves describing the extraction yield dynamics for different working parameters has a similar shape with those characterizing a process with diffusive control. All these observations lead to the conclusion that the shrinking core model is adequate for mathematical process characterisation. A new paper considering the process modelling and model parameters investigation is in progress. The consideration of surface resistance at oil dissolving core will be the novelty of the model characterising the process evolution at particle level.

Acknowledgements

The authors would like to acknowledge Eng. Adrian Radu (ICECHIM-Romania) for his laboratory assistance for GC analysis.

REFERENCES

[1] *P. Jolivet, C. Deruyffelaere, C. Boulard, A. Quinsac, R. Savoire, N. Nesi and T. Chardot*, "Deciphering the structural organization of the oil bodies in the *Brassica napus* seed as a mean to improve the oil extraction yield", in Industrial Crops and Products, **vol. 44**, Jan. 2013, pp. 549-557

[2] *C. Banu*, Manualul inginerului de industrie alimentară, (Handbook of Food Engineer), Editura Tehnică, Bucureşti, 1999, **vol. 2**, pp. 1182-1188

[3] *Y. Li, B. A. Watkins*, "Current Protocols in Food Analytical Chemistry", in John Wiley and Sons Inc. Edition, New York, 2001, pp. D1.2.1-D1.2.15

[4] *E. E. Perez, A. A. Carelli and G. H. Crapiste*, "Temperature-dependent diffusion coefficient of oil from different sunflower seeds during extraction with hexane", in Journal of Food Engineering, **vol. 105**, no. 1, Jul. 2011, pp. 180-185

[5] *I. A. Kartika, P. Y. Pontalier and L. Rigal*, "Twin-screw extruder for oil processing of sunflower seeds: Thermo-mechanical pressing and solvent extraction in a single step", in Industrial Crops and Products, **vol. 32**, no. 3, Nov. 2010, pp. 297-304

[6] *R. L. Almeida, M. A. S. S. Ravagnani and A. N. Modenes*, "Soybean oil extraction in belt extractors with miscella recirculation", in Chemical Engineering and Processing: Process Intensification, **vol. 49**, no. 10, Oct. 2010, pp. 996-1005

[7] *H. Sovová*, "Rate of the vegetable oil extraction with supercritical CO_2 - I. Modelling of extraction curves", in Chemical Engineering Science, **vol. 49**, no. 3, 1994, pp. 409-414

[8] *H. Sovová, J. Kučera and J. Jež*, "Rate of the vegetable oil extraction with supercritical CO_2 - II. Extraction of grape oil", in Chemical Engineering Science, **vol. 49**, no. 3, 1994, pp. 415-420

[9] *C. Marrone, E. Poletto, E. Reverchon and A. Stassi*, "Almond oil extraction by supercritical CO_2: experiments and modelling", in Chemical Engineering Science, **vol. 53**, no. 21, Nov. 1998, pp. 3711–3718

[10] *C. Banu*, Tratat de Chimia Alimentelor, (Treaty of Food Chemistry), Editura Agir, Bucureşti, 2002, pp. 323-324

[11] *M. Iordan*, Industrii Alimentare Extractive, Tehnologia uleiurilor vegetale, (Extractive Food Industry, Vegetable Oils Technology), Editura Macarie, Târgovişte, 2002, pp. 127-130

[12] *E. Vlad., C. S. Bildea, V. Plesu, G. Marton and G. Bozga*, "Design of Biodiesel Production Process from Rapeseed Oil", in Rev. Chim., **vol. 61**, no. 6, 2010, pp. 595-603

[13] *F. D. Gunstone*, "Rapeseed and Canola Oil: production, processing, properties and uses", in CRC Press LLC, 2004, pp. 17-37

[14] *L. M. Rumac*, Tehnologia uleiurilor vegetale şi volatile, (Vegetal and Volatile Oils Technology), Universitatea "Politehnica" din Timişoara, 1995, pp. 8-9

[15] *A. Ajchariyapagorn, T. Kumhom, S. Pongamphai, S. Douglas, P. L. Douglas and W. Teppaitoon*, "Predicting the extraction yield of nimbin from neem seeds in supercritical CO_2 using group contribution methods, equations of state and a shrinking core extraction model", in The Journal of Supercritical Fluids, **vol. 51**, no. 1, Nov. 2009, pp. 36-42

[16] *W. L. Hsu, M. J. Lin and J. P. Hsu*, "Dissolution of Solid Particles in Liquids: A Shrinking Core Model", in International Journal of Chemical and Biological Engineering, **vol. 2**, no. 4, 2009, pp. 205-210.