NOVELBALTIC

Market driven authentic non-timber forest products from the Baltic Sea region

Non-Timber Forest products
WP6 - Conceptual design of selected NTFP processes

O6.2. Material and energy balances

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Elham Khalati
Pekka Oinas

AALTO UNIVERSITY

School of Chemical Engineering

Abstract

The object of this report is to present the mass and energy balance calculations per batch extraction of selected plants and represent block flow diagrams of raw material pre-treatment and supercritical fluid (SFE) extraction process using carbon dioxide as the solvent. In comparison to conventional techniques such as solvent extraction, supercritical extraction is a more efficient and sustainable method. Besides, SFE with carbon dioxide offers other advantages including a small amount of organic solvent or no solvent, high mass transfer rates at relatively low temperatures, selective extraction, and inexpensive operating/running cost. [1]–[3]

In the proposed process essential oils and extracts are obtained from three plants: Garden angelica (*Angelica archangelica)*, roseroot *(Rhodiola rosea)* and maral root (*Rhaponticum carthamoides)*. The corresponding products from supercritical extraction are angelica root essential oil, salidroside/rosavin rich extract and 20-hydroxyecdysone rich extract. The extracted products in question, essential oils, having adaptogenic features can be widely used in dietary supplements, cosmetics and medical applications.

The maximum operating condition during the supercritical fluid extraction (SFE) with carbon dioxide is 80 ℃ and 280 bar in the extractor, well above the supercritical point of carbon dioxide. The average yield of the SFE based on 3-hour dynamic extraction is 0.2 % for garden angelica, 5.6 % for roseroot and 1.1 % for maral root. In this research, constant solvent flow was considered as the scale-up factor, and other properties including porosity, length to diameter ratio of the extractor, and particle shape and diameter were assumed to be similar to the lab-scale process.

In this process, roots of *roseroot* and *maral root* are to be dried before the extraction; however, due to the heat-sensitivity of *garden angelica*, it is to be kept fresh for extraction. The whole process is based on two sections, pre-treatment step and extraction unit.

The total annual production capacity of the plant is 4000 kg based on 725 batches of supercritical CO_2 extraction per year.

Contents

1. Definition of the selected process

This report on the non-timber forest products (NTFP) production focuses on the definition of the selected process, specification of raw materials and products, block flow diagram (BFD), process description, and mass and energy balance. The basis of the process has been reported in earlier NTFP report series. The essential that have been investigated, can be used e.g. for dietary supplements, cosmetics and medicinal applications.

The supercritical CO_2 extraction process is compared with the conventional solvent extraction technique in Table 1 by 5 aspects: capital and operating costs, sustainability, efficiency, versatility and selectivity, and maturity. Based on the literature review, although the capital cost of the supercritical extraction is higher than conventional methods, its reasonable operating/running costs makes it a viable technique also in large-scale production. During the past 20 years, the supercritical extraction approach has been employed with or without a fraction of co-solvent to harvest a vast range of extracts from oleoresin, essential oils, groups of bioactive compounds (alkaloids, terpenes, and phenolic), and single compounds. [3] The method also brings about the possibility of minimizing or not using the organic solvent, thereby avoiding the need for incineration which is an environmentally hazardous and expensive process. Although supercritical extraction is a popular method in lab-scale processes, due the maturity point of view, it has not been used commercially as much as other conventional techniques. [4]–[6] However, according to Table 1, SFE with CO_2 can be considered as a suitable method for commercial applications as well.

Table 1. Comparison of SFE with CO_2 with conventional solvent extraction

Criterion	Weight	Score (1-10)	
		SFE with CO_2	Solvent extraction
Capital and operating cost	5	5	7
Sustainability	4	8	3
Efficiency	4	6	5
Versatility and selectivity	3	7	4
Maturity	3	5	8
Total score		117	103

The products of the process are essential oil and extracts containing different active ingredients from the three herbs, the main substances are angelica root oil from Angelica archangelica (garden angelica) fresh shredded roots, salidroside and rosavin extracts from Rhodiola rosea (roseroot) dried ground roots, and 20-hydroxyecdysone extract from Rhaponticum carthamoides (maral root) dried ground roots.

This report is a continuation of the earlier reports in the NTFP report series where shortly a justification for the suggestion for investment decision regarding chosen process and products was presented.

2. Process design

2.1. Block flow diagram

In this process, the fresh raw materials are directly collected from the farm after harvesting, and therefore, they have to be pre-treated before the main extraction. The pre-treatment step includes prewashing, cutting, washing, dewatering, shredding, drying and grinding. Due to the heat sensitivity of garden archangelica, it should not be addressed to higher temperatures and thus, processed as such. Figure 1 shows the block flow diagram of the pre-treatment step. After the pretreatment of the raw materials, they are loaded into the extractor. According to Lehto et al. [7] the total water consumption for washing of plant roots is 1.5 m^3 per ton of the plant roots. In this process, the air dryer operating temperature is 40 °C and its dehydration capacity of the air dryer is 69 kg/h.

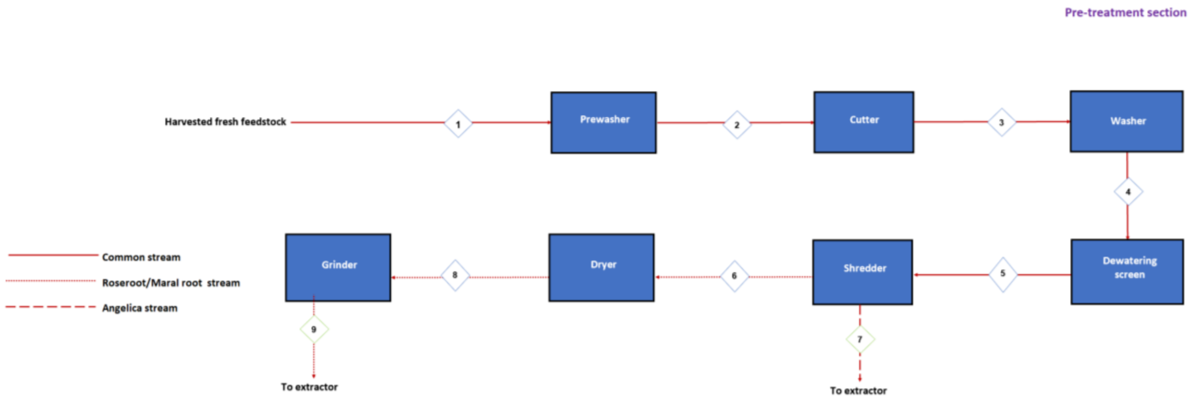

Figure 1. Different sections of the pre-treatment step for garden angelica, roseroot, and maral root.

For having an efficient extraction from roseroot and maral root a co-solvent, such as ethanol, can be injected to the supercritical CO_2 stream. However, for retrieving essential oil from roots of garden angelica pure SC-CO_2 is used. Generally, the main steps of the extraction process are the following: 1) extraction of intended compounds with supercritical CO_2, 2) co-solvent and solvent recovery, and 3) separaton the main product. In the case of garden angelica, the extracted fatty acids are first separated from the main process, and then the solvent is recovered. Figure 2 represents the block flow diagram of the extraction process. It is worth mentioning that other than ethanol, other types of co-solvents may also be used in this process depending on the composition of the raw material.

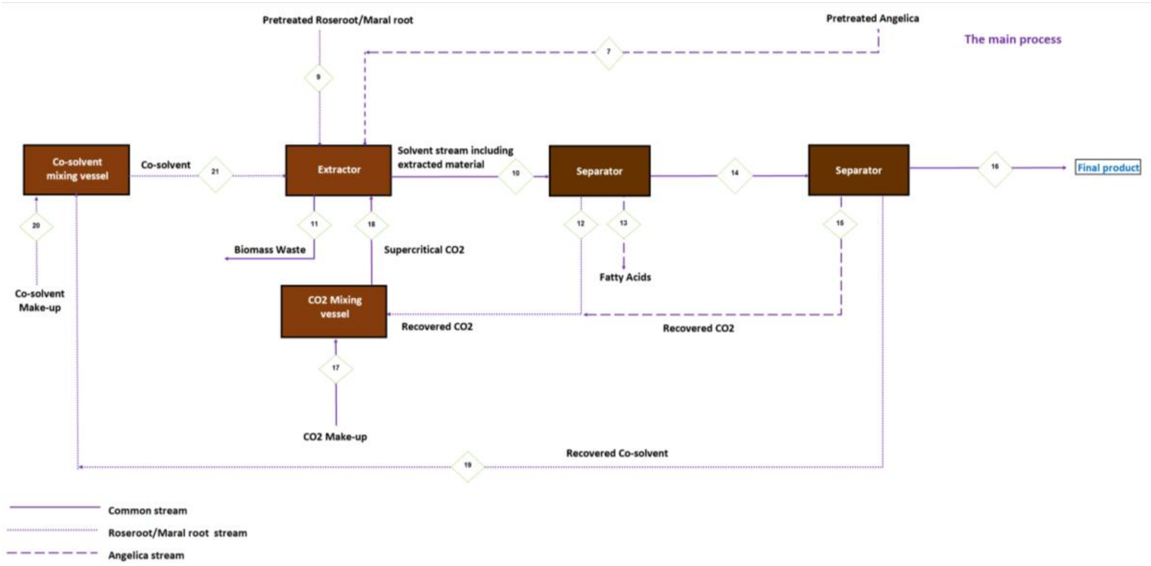

Figure 2. Different sections of the main extraction process for roots of fresh Angelica, dried Roseroot, and dried Maral root

In the following, the capacity, production, and details of the scaled process for each selected plant, garden angelica (Angelica archangelica), roseroot (Rhodiola rosea) and maral root (Rhaponticum carthamoides), are explained.

2.2. Production and capacity

The production is spread between the plants in order to protect the continuity of the production based on the suitable harvesting time for each plant. Table 2 shows the monthly distribution of production. The extraction process plant is operated in two shifts and the process is batch type. 3 batches are performed daily. In each batch, the extraction process takes about 3 hours, and 1 hour is required for cleaning, reloading, and pressurizing the equipment.

According to Table 2, the total yearly production time for the essential oil is 4 months; as a result, based on daily 3 batches of extraction, 21 working days per month, and 200 kg loading capacity of the extractor, the annually required fresh garden angelica root is as follows:

$$200 \frac{kg}{batch} x\ 3\ \frac{batch}{d} x\ 21\ \frac{d}{mth}\ x\ 4\ \frac{mth}{a} = \ 50400\ kg/a \qquad (1)$$

Fresh roseroot and maral root are required to be dried first to the point that the residual moisture is 5 %. According to Galambosi et al. [8] and Zomborszki et al. [9], the water content in fresh roseroot plants is about 78 %. Hence, in order to provide 200 kg of the dried feedstock for each batch process, appr. 860 kg of fresh roseroot is required. As a result, the total required fresh roseroot will be

$$0.86\ \frac{tonnes}{batch} x\ 3\ \frac{batch}{d} x\ 21 \frac{d}{mth} x\ 5\ \frac{mth}{a} = 270\ \ t/a \qquad (2)$$

The water content of fresh maral root is about 75 %, and 760 kg of the fresh plant has to be dehydrated to gain 200 kg of dried maral root.[10] The yearly consumed fresh maral root is

$$0.76\ \frac{tonnes}{batch} x\ 3\ \frac{batch}{d} x\ 21 \frac{d}{mth} x\ 2.5\ \frac{mth}{a} = 120\ \ t/a \qquad (3)$$

Additionally, half a month is reserved for the maintenance work. Based on the research, yields of 0.2 % of essential oil from fresh root of garden angelica, 5.6 % of extract from the dried root of roseroot and 1.1 % of extract from the dried root of maral root have been considered. Based on the considered assumptions the annual production plant capacity is approximately 4 tons of products from the three plants. [11]–[13]

Table 2. Monthly distribution of the product

Product	July	August	September	October	November	December	January	February	March	April	May	June
Angelica root oil												
Roseroot extract												
Marsl root extract												

2.3. Process simulation and description

In this process, the software Aspen Plus™ was used to simulate and design the scaled process plant and develop the energetic model. The choice of a suitable activity coefficient model and equations of state was very critical since there is equipment working at a large range of operating pressure, from 1 to 280 bar. [14]

For estimating the capacity of each equipment, roseroot was considered to be the main criterion since it owns the largest share of the total feedstock. As mentioned before, due to the fact the fresh material cannot be stored at ambient temperature for a long time after harvesting, they have to be dried immediately. Therefore, for roseroot and maral root, the pretreatment step is completely independent of the main extraction process. For garden angelica, pre-treatment and extraction processes are performed consecutively on the same day.

2.4. Mass balance

Figures 3 to 5 represent the mass balances for roseroot, maral root, and garden angelica, respectively. The yields of essential oils had to be assumed from literature sources. Here, the considered extract yields were 0.2 %, 5.6 % and 1.1 %, from fresh garden angelica root, dried roseroot and dried maral root, respectively. For the main extraction process and the pretreatment section, all mass balances are made based on the capacity (load) of the batch extractor device, 200 kg, and its equivalent required fresh material for each plant. The CO_2 and ethanol recovery are in the range of 97-98 % and 94-96 %, respectively, based on estimated losses in extraction and separators. The mass balances are based on the experimental yields of desired products and estimations of essential oil concentrations in fresh roots. As the very extraction process is carried out batchwise, the mass balance is also batch-based.

Besides, constant velocity of CO_2 was used as the scaling factor to calculate the mass flow of the supercritical CO_2 in the commercialized extraction process using the lab-scale experimental data. Other properties including porosity, length to diameter ratio of extractor, and particle shape and diameter were assumed to be the same as the lab-scale plant to get more accurate results. The co-solvent content as carbon dioxide percentage is 10 % and 7.1% for roseroot and maral root, respectively. Table 3 shows the mass flow rate of CO_2 and co-solvent for roseroot, maral root, and garden angelica. The stream numbers are based on the block flow diagrams shown in Figures 1 and 2. The total mass of CO_2 and ethanol is calculated based on the total extraction time per batch process which is 3 hours.

The material balance figures for the three plants: roseroot, maral root and garden angelica, are presented in Tables 4-6.

Table 3. Mass flow rate of CO_2 and co-solvent related to the three plant raw materials.

Plant raw material	CO_2 mass flow (kg/h)	Ethanol mass flow (kg/h)
Garden angelica (fresh)	107	-
Roseroot (dried)	632	63.2
Maral root (dried)	107	7.6

Table 4. Material balance figures of roseroot pretreating and extraction.

Roseroot																					
Component	**Stream**																				
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
Total mass (kg)	864	864	864	864	864	864	0	200	200	2097	189	1877	0	161	0	**15**	57	1934	145	7	152
CO2 (kg)	0	0	0	0	0	0	0	0	0	1896	0	1839	0	1	0	**0,17**	57	1896	0	0	0
Ethanol (kg)	0	0	0	0	0	0	0	0	0	190	0	38	0	148	0	**3,21**	0	38	145	7	152
Biomass (kg)	177	177	177	177	177	177	0	177	177	0	177	0	0	0	0	**0**	0	0	0	0	0
Extract (kg)	12,5	12,5	12,5	12,5	12,5	12,5	0	12,5	12,5	11,2	1,3	0	0	11,2	0	**11,20**	0	0	0	0	0
Water (kg)	674	674	674	674	674	674	0	10	10	0	10	0	0	0	0	**0**	0	0	0	0	0
Fatty acid (kg)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**0**	0	0	0	0	0
Temperature (℃)	20	20	20	20	20	20	-	24	20	60	20	14	-	95	-	**30**	14	80	52	20	80
Pressure (bar)	1	1	1	1	1	1	-	1	1	35	1	50	-	1	-	**1**	50	200	1	1	200

Table 5. Material balance figures of maral root pretreating and extraction.

Maral root																					
Component	**Stream**																				
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
Total Mass flow	760	760	760	760	760	760	0	200	200	346	198	319	0	18	0	**3**	8	327	15	1	16
CO2 (kg)	0	0	0	0	0	0	0	0	0	321	0	313	0	0	0	**0**	8	321	0	0	0
Ethanol (kg)	0	0	0	0	0	0	0	0	0	23	0	6	0	16	0	**0,84**	0	6	15	1	16
Biomass (kg)	179	179	179	179	179	179	0	179	179	0	179	0	0	0	0	**0**	0	0	0	0	0
Extract (kg)	11	11	11	11	11	11	0	11	11	2,2	8,3	0	0	2,2	0	**2,2**	0	0	0	0	0
Water (kg)	570	570	570	570	570	570	0	10	10	0	10	0	0	0	0	**0**	0	0	0	0	0
Fatty acid (kg)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**0**	0	0	0	0	0
Temperature (℃)	20	20	20	20	20	20	-	24	20	60	20	14	-	95	-	**30**	14	60	52	20	60
Pressure (bar)	1	1	1	1	1	1	-	1	1	35	1	50	-	1	-	**1**	50	280	1	1	280

Table 6. Material balance figures of garden angelica pretreating and extraction.

Angelica																					
Component	**Stream**																				
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
Total Mass flow	200	200	200	200	200	0	200	0	0	322	199	0	0,19	321	313	**0,40**	8	321	0	0	0
CO2 (kg)	0	0	0	0	0	0	0	0	0	321	0	0	0,05	321	313	**0**	8	321	0	0	0
Ethanol (kg)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**0**	0	0	0	0	0
Biomass (kg)	49	49	49	49	49	0	49	0	0	0	49	0	0	0	0	**0**	0	0	0	0	0
Essential oil (kg)	0,70	0,70	0,70	0,70	0,70	0	0,7	0	0	0,4	0,3	0	0	0,4	0	**0,40**	0	0	0	0	0
Water (kg)	150	150	150	150	150	0	150	0	0	0	150	0	0	0	0	**0**	0	0	0	0	0
Fatty acid (kg)	0,25	0,25	0,25	0,25	0,25	0	0,25	0	0	0,14	0,11	0	0,14	0	0	**0**	0	0	0	0	0
Temperature (℃)	20	20	20	20	20	-	20	-	-	60	20	-	30	1	14	**20**	14	40	-	-	-
Pressure (bar)	1	1	1	1	1	-	1	-	-	60	1	-	1	35	50	**1**	50	120	-	-	-

2.5. Energy balance

In this process, the main utilities in this process, the utilized utilities are electricity, cooling water, low pressure (LP) steam, and aqueous 50 % propylene glycol (PG) solution as a refrigeration medium. Tables 7-9 show the utility consumption and prices per batch process for roseroot, maral root and garden angelica. The electricity consumption includes the energy consumption of pumps and the required energy for electrical heating.

Table 7. Utility consumption and the related price per batch of refining dried roseroot extract

Utilities	Consumption	Price	Unit	Total price
	unit/batch	€/unit		€/batch
Electricity	0.3	80 [15]	MWh	24
Cooling water	7	5	m^3	35
LP steam	0.28	20	ton	5.6
50 % PG	0.66	6.9 [16]	GJ	4.6

Table 8. Utility consumption and the related price per batch of refining dried maral root extract

Utility	Consumption	Price	Unit	Total price
	unit/batch	€/unit		€/batch
Electricity	0.23	80	MWh	18.4
Cooling water	0.75	5	m^3	3.8
LP steam	0.044	20	ton	0.9
50 % PG	0.18	6.9	GJ	1.2

Table 9. Utility consumption and the related price per batch of refining fresh garden angelica extract

Utility	Consumption	Price	Unit	Total price
	unit/batch	€/unit		€/batch
Electricity	0.005	80	MWh	0.4
Cooling water	0	5	m^3	0
LP steam	0.035	20	ton	0,7
50 % PG	0.09	6.9	GJ	0.62

3. Conclusions

In this report, material and energy balance calculations per batch extraction of essential oils of selected plants: Garden angelica (*Angelica archangelica)*, roseroot *(Rhodiola rosea)* and maral root (*Rhaponticum carthamoides)*, are presented. The corresponding products from supercritical extraction are angelica root essential oil, salidroside/rosavin rich extract and 20-hydroxyecdysone rich extract.

These extracted products having adaptogenic features can be used used widely in dietary supplements, cosmetics and medicinal applications. The extraction method selected for this investigation is a high-pressure extraction with carbon dioxide at supercritical conditions as the solvent. Supercritical extraction appears to be an efficient and sustainable method due to the use of non-toxic carbon dioxide for this kind of extraction. Besides, supercritical extraction with carbon dioxide offers other sustainable advantages including a small amount of organic solvent or no extra solvent, high mass transfer rates at relatively low temperatures, selective extraction, uncomplicated solvent recycle and inexpensive operating cost. The total annual production capacity of the designed plant of 4000 kg based on 725 batches was resulted.

References

[1] T.M. Attard, C.R. McElroy, A.J. Hunt, “Economic assessment of supercritical CO_2 extraction of waxes as part of a maize stover biorefinery” *Int. J. Mol. Sci.* 16(8), 2015, pp. 17546-64. doi: 10.3390/ijms160817546.

[2] G. Anitescu, C. Doneanu, V. Radulescu, “Isolation of coriander oil: Comparison between steam distillation and supercritical CO_2 extraction” *Flavour Fragr. J.* 1997. doi: 10.1002/(SICI)1099-1026(199705)12:3<173::AID-FFJ630>3.0.CO;2-1.

[3] K.Y. Khaw, M.O. Parat, P.N. Shaw, J.R. Falconer, “Solvent supercritical fluid technologies to extract bioactive compounds from natural sources: A review”, *Molecules 22(7), 2017, 22 p.* doi: 10.3390/molecules22071186.

[4] G. L. Zabot, M. N. Moraes, M.A.A. Meireles, “Supercritical fluid extraction of bioactive compounds from botanic matrices: Experimental data, process parameters and economic evaluation”, *Recent Patents Eng.* 6(3), 2012, pp. 182-206. doi: 10.2174/187221212804583204.

[5] J.M. Prado, I. Dalmolina, N.D.D. Cararetoa, R.C. Bassoa, A.J.A. Meirellesa, J.V. Oliveira, E.A.C. Batista, M.A.A. Meireles, “Supercritical fluid extraction of grape seed: Process scale-up, extract chemical composition and economic evaluation” *J. Food Eng.* 109 (2), 2012, pp. 249-257. doi: 10.1016/j.jfoodeng.2011.10.007.

[6] M.M.R. de Melo, A.J.D. Silvestre, C.M. Silva, “Supercritical fluid extraction of vegetable matrices: Applications, trends and future perspectives of a convincing green technology,” *J. Supercrit. Fluids* 92, 2014, pp. 115-176. doi: 10.1016/j.supflu.2014.04.007.

[7] M. Lehto, I. Sipilä, L. Alakukku, H-R. Kymäläinen, “Water consumption and wastewaters in fresh-cut vegetable production,” *Agric. Food Sci.* 23, 2014, pp. 246-256. doi: 10.23986/afsci.41306.

[8] Z. Péter Zomborszki, N. Kúsz, D. Csupor, W. Peschel, “Rhodiosin and herbacetin in Rhodiola rosea preparations: additional markers for quality control?” *Pharm. Biol.* 57(1), 2019, 295–305. doi: 10.1080/13880209.2019.1577460.

[9] M.G. Thomsen, B. Galambosi, Z. Galambosi, M. Uusitalo, R. Mordal, A. Heinonen, “Harvest time and drying temperature effect on secondary metabolites in Rhodiola rosea” *Acta Hortic.* 955, 2012. doi: 10.17660/ActaHortic.2012.955.35.

[10] E. Skała, A. Kicel, M.A. Olszewska, A.K. Kiss, H. Wysokińska, “Establishment of hairy root cultures of rhaponticum carthamoides (Willd.) Iljin for the production of biomass and caffeic acid derivatives” *Biomed Res. Int.* 2015, pp. 181098-181098. doi: 10.1155/2015/181098.

[11] P. Iheozor-Ejiofor,E.S. Dey, “Extraction of rosavin from Rhodiola rosea root using supercritical carbon dioxide with water”, *J. Supercrit. Fluids* 50(1), 2009, pp. 29-32. doi: 10.1016/j.supflu.2009.04.011.

[12] H. Sovová, L. Opletal, M. Sajfrtová, and M. Bártlová, “Supercritical fluid extraction of cynaropicrin and 20-hydroxyecdysone from Leuzea carthamoides DC”, *J. Sep. Sci.* 31(8), 2008, pp. 1387-92. doi: 10.1002/jssc.200700496.

[13] C. Doneanu and G. Anitescu, “Supercritical carbon dioxide extraction of Angelica archangelica L. root oil” *J. Supercrit. Fluids* 12(1), 1998, pp. 59-67. doi: 10.1016/S0896-8446(97)00040-5.

[14] J.Q. Albarelli, D.T. Santos, M.J. Cocero, M.A.A. Meireles, “Economic analysis of an integrated annatto seeds-sugarcane biorefinery using supercritical CO_2 extraction as a first step”, *Materials* 9(6), 2016, doi: 10.3390/ma9060494.

[15] Statistics Finland, “Energy prices [e-publication]”, Helsinki 2020. [Online]. Available: http://www.stat.fi/til/ehi/2020/03/ehi_2020_03_2020-12-10_kuv_005_en.html.

[16] R. Turton, J.A. Shaeiwitz, and D. Bhattacharyya, W.B Whiting, *Analysis, Synthesis and Design of Chemical Processes*, 4th Ed., Pearson 2018.