

Supercritical extraction of plant material with carbon dioxide. Scaling up from laboratory to 1/4 technical scale

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Introduction

Extraction is a diffusive process of exchanging mass, used for the separation of elements from mixtures of solids and liquids. An element from the extracted phase moves to the solvent as a result of concentration differences until it reaches a state of equilibrium.

Supercritical extraction is a special type of solvent extraction in which the role of the solvent is played by the liquid which is above critical temperature and pressure. Under supercritical conditions, the physical and chemical parameters of the liquid reach intermediate values between the gaseous and liquid state and are characterized by low viscosity at a relatively large density and high values of the diffusion coefficient. Because of this, supercritical liquids have good penetration and transport properties and are suitable for use as solvents in extraction processes. Changes in pressure and temperature with regard to supercritical parameters considerably change their solvency and selectivity [1, 2].

In certain cases, a continuous stream of liquid solvent, referred to as entrainer, is added to the gas stream. A proper selection of the entrainer may considerably increase the rate and selectivity of extraction. Evaporation of the entrainer may be obtained through determining the proper working temperature of the separator receiving the extract.

Carbon dioxide is very often used for separating elements from permanent plant materials. Carbon dioxide is physiologically inert and does not react with the majority of natural substances and is easily separated from the extracted product. Moreover, it has bacteriostatic properties; it is incombustible, cheap and easily accessible. Industrial scale processes are conducted with its full recirculation.

Another important reason for using supercritical extraction for isolating substances from plant materials is that extracts obtained via CO₂ extraction do not contain solvent residues, which is often the case with classic solvent extractions. Furthermore, organic solvents and the temperature used in classic solvent extraction may cause the decrease or even loss of the extracted elements' active properties.

The mentioned advantages of carbon dioxide as a solvent in supercritical extraction contribute to its application in extractions whose products are intended for use in the pharmaceutical, cosmetic and food industry.

The application of extraction via supercritical and liquid CO₂ for secreting oil from linseed has been presented in numerous publications. Some of them tested the influence of pressure, material break-up and CO₂ flow on the rate and capacity of the process, while in certain cases experimental results were compared with the results obtained by means of calculations using mathematical models of the process [3 ÷ 5]. Other publications presented tests which compared the capacity of linseed oil extraction using supercritical CO₂, conducted under different temperature and pressure conditions, with classic solvent extractions using petroleum ether [6] and hexane [7].

Supercritical extraction of dried tea leaves using CO₂ was discussed in a patent which described a multi-variant extraction process in which, depending on the extraction parameters and the used entrainer, different end products were obtained [8]. These products were decaffeinated tea leaves, caffeine, tea aroma and polyphenols.

The variety of plant materials and the changing physical and chemical parameters of obtained extracts require a separate determination of extraction conditions for each case. Besides extraction parameters such as the process's pressure and temperature, the manner of receiving the extract itself may also prove to be a significant factor. When conducting the batch extraction to the end in order to eliminate all the elements from the material, the obtained extract changes its composition, density and viscosity. In certain cases, at the end of the extraction process and in conditions of extraction reception it may be a semi-solid or solid body.

The available literature does not provide examples of CO₂ supercritical extraction of linseed cake which constitutes the residue of pressing oil from linseed, nor does it contain descriptions of green tea leaves' extraction which leads to a complete isolation of all elements. For this reason, the process parameters for both these cases had to be determined via experiments.

This work presents the results of linseed cake and dried green tea leaves extraction using CO₂, on a lab scale and 1/4 technical scale.

Experimental part

The extraction trials performed on a laboratory scale contributed to determining the optimum temperature of the process and showed the influence of using ethanol and methanol as entrainers. The results obtained on a laboratory scale were then used to increase the process scale and to perform extraction via CO₂ on a 1/4 technical scale.

Materials and reagents

In the experiments, extraction was performed on plant materials, i.e. linseed cakes and dried green tea leaves.

The linseed cakes came from oil manufacturing plants and they constituted typical production waste from lines for pressing oil from linseed, used as an additive to fodder.

The amount of oil substances in the cakes has been determined during extraction using toluene at boiling point and equaled approx. 10 ÷ 12% by weight.

The dried green tea leaves of a commercial name "Gun Powder" were obtained from the Natur-Vit Herbal Industry Plants in Pińczów. This tea belongs to a type of green tea imported in wholesale packs and batched at the plant.

Prior to the extraction, both plant materials were grinded using a percussive mill, thus obtaining a grain break-up below 0.75 mm.

The extraction used carbon dioxide from the Messer Polska company in Chorzów, as well as entrainers in the form of 95% rectified spirit from the Lubelskie Spirit Plants and analytically pure methanol from the Chempur company.

Apparatus for supercritical extraction and conducting experiments

Figure 1 presents a simplified installation diagram for testing supercritical extraction processes. The process line of the laboratory

apparatus differed from the 1/4 technical apparatus only in the size of the apparatus, scope of measuring instruments and the manner of solving the extractor heating.

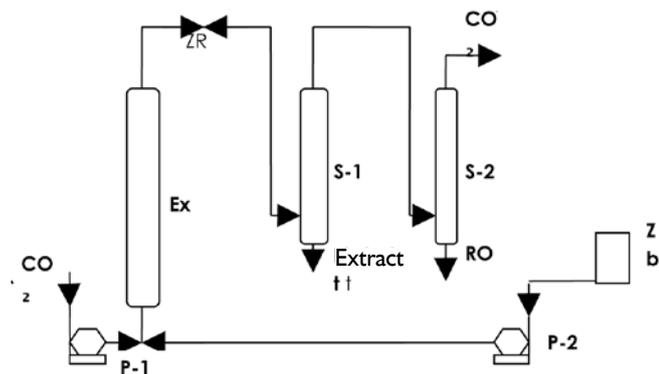


Fig. 1. Scheme of apparatus for supercritical extraction

After placing a weighed amount of the broken-up plant material in the extractor Ex and determining the pressure of the process, a solvent was fed to the extractor using pump P-1. The pump was fitted with a pressure gauge and worked with the pressure regulation circuit. An EV expansion valve was placed on the outlet piping from the extractor, which maintained pressure in the extractor. The pressure-free receiving node consisted of separators S-1 and S-2 and a unit for measuring the amount of the gaseous solvent, not presented in Figure 1. The temporary flow was measured using a rotameter, and the total amount - using a gas flowmeter. The extract was collected to glass containers placed inside separator S-1, while the volatile products (mainly the entrainer) were gathered in glass containers placed inside separator S-2. The S-2 separator was cooled down to a temperature of -30°C. The entrainer stream was fed from the Sc storage container to the inlet piping of the extractor using a pressure metering pump P-2.

The volume of the extractor of the lab apparatus equaled approx. 150 cm³, while the volume of the S-1 and S-2 separators - approx. 50 cm³. In the 1/4 technical installation the 10 dm³ extractor worked with S-1 and S-2 separators whose volume equaled 1 dm³.

During the experiments the tapping of the extract was interrupted after each working day and was resumed on the following day.

Analysis of test results

Because of the scale of the conducted process, the description and analysis of results was divided into laboratory and 1/4 technical tests. In each of the scales the extraction of linseed cakes and green tea leaves was presented separately.

Laboratory scale

Extraction tests performed on a laboratory scale with the aim of determining the most favorable process temperature were conducted under a pressure of 20 MPa and with a CO₂ flow of 40 ÷ 60 dm³/h. In order to compare the obtained data, the experiment results were converted into the plant material feed with a mass of 100 g, while the extract mass increments were related to the flow times of the same volumes of the applied carbon dioxide. Subsequent experiments were conducted using ethanol and, in the case of linseed cakes, methanol as the entrainer, checking their effect for the temperature in which the process occurred the fastest.

a) Linseed cakes

The rate of the process of linseed cake extraction using CO₂ was tested for the temperatures of 27°C, 40°C, 60°C and 80°C. In the experiment with a temperature of 27°C, i.e. lower than the critical temperature of carbon dioxide (T_k CO₂=31.05°C), the solvent remained in liquid phase.

In the extraction trial of linseed cakes, conducted under a temperature of 35°C and a pressure of 20 MPa, methanol was used as the entrainer; it was fed to the carbon dioxide stream in a continuous manner in the amount of 2 cm³/h. The results of the conducted experiments are included in Table 1.

Table 1

Extraction experimental data for linseed cake - laboratory scale

Temperature									
27°C		40°C		60°C		80°C		35°C / with ethanol 2 cm ³ /h	
Time h	Cumulative amount of the extract g	Time h	Cumulative amount of the extract g	Time h	Cumulative amount of the extract g	Time h	Cumulative amount of the extract g	Time h	Cumulative amount of the extract g
6.5	2.2849	7.5	1.6522	11	1.0483	6.25	0.2293	5.5	3.2448
10.25	3.3716	15	3.6736	16	1.6568	14.75	0.5973	10.75	6.6895
15.75	5.1605	21.75	5.6277	23	2.5920	23.25	0.9150	16.25	9.5957
21.25	6.6675	29	7.2317	30.5	3.4803	31.75	1.1428	23.5	10.1323
28.75	8.3415	34.5	*7.7325	37	4.3092	40.25	1.3491	29	10.1675
35	*8.5355			44	4.8790	46.75	1.5153		
				51	5.4225	54.5	*1.6988		
				57	5.9397				
				63	6.4198				
				68	6.9419				
				74	7.5755				
				82	8.4161				
				90	9.1860				
				97	9.8215				
				104	10.2467				
				112	10.4277				
				118	10.4485				

* - extraction was not carried out until the end

A graphic representation of the extraction process in the conducted experiments was presented in Figure 2.

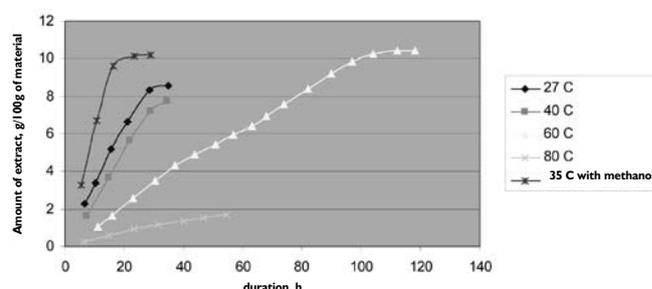


Fig. 2. Extraction velocity for linseed cake - laboratory scale

The results of extracting raw linseed cakes using CO₂ show that the rate of the process depends to a large degree on the temperature. In the performed extraction trials of raw linseed cakes, the highest process rate was obtained near the critical temperature of carbon dioxide, i.e. within the temperature scope of 27-35°C. This rate increased by approx. 30% after using methanol as the entrainer. Analyzing the

obtained graphs, it is clearly visible that at a temperature of 60°C the extraction occurred four times slower compared to the process carried out at a temperature of 27°C. In extraction carried out until the end (under temperature of 60°C and 35°C with an entrainer), until the disappearance of the extract stream, the capacity of the process equaled over 10% and was comparable to classic solvent extractions.

Based on the attempts to extract linseed cakes on a laboratory scale it was decided to carry out the extraction on a larger scale using supercritical CO₂ at a temperature of 35°C, using an entrainer.

b) Green tea

In order to assess the influence of temperature on the rate of the process of extracting green tea leaves using CO₂, extraction trials were conducted at a temperature of 35°C, 40°C and 60°C. The experiments were carried out under a pressure of 20 MPa until the disappearance of the extract in the CO₂ stream, and the obtained results were presented in Table 2.

Table 2

Extraction experimental data for green tea leaves (amount of extract for 100 g of material) - laboratory scale

Extraction temperature, °C	35	40	60
Extraction time, h	24	24	24.5
Amount of extract, g	1.8234	2.1894	2.0834

Because of the similar amounts of extract tapped in extractions conducted at a temperature of 40°C and 60°C, attempts with ethanol entrainer were performed at a temperature of 35°C and 40°C. Prior to the extractions, 5 cm³ of ethanol was added to the material. During the process, an entrainer was fed to the carbon dioxide in a continuous manner, in the amount of 2 cm³/h. The experiment results converted into 100 g of material and the CO₂ flow in the amount of 55 dm³/h were presented in table 3.

Table 3

Extraction data – trials with adding organic solvent for green tea leaves - laboratory scale

Temperature			
35°C		40°C	
Time h	Cumulative amount of extract g	Time h	Cumulative amount of extract g
6	0.8807	6.5	1.0459
12	1.3686	13	1.5789
18	1.6652	19.5	1.9577
24	1.8554	26	2.1907
30	2.0162	34.5	2.3851
36	2.0492	41	2.5509
42	2.1807	49	2.6913
48	2.3410	54.5	2.7498
56	2.3980	60	2.8622
62	2.4400	66.5	3.0806
68	2.5398		
74	2.6121		
80	2.6773		
86	2.7092		
93.25	2.9546		

A graphic representation of the extraction of green tea using an entrainer was presented in Figure 3.

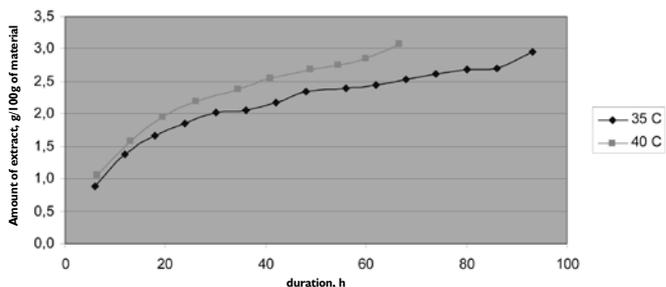


Fig. 3. Velocity of supercritical extraction for tea leaves with adding organic solvent - lab. scale

During the extraction of green tea leaves difficulties occurred with tapping after the 20th hour of the process. The reason for this was the semi-solid extract depositing in the expansion valve and inlet piping of the S-I separator which blocked the flow. The use of ethanol as the entrainer did not increase the rate of the process but it did enable the tapping of the extract until the end of the process. Results of the 24-hour extractions conducted at various temperatures showed that the most favorable one, because of the rate of the process, turned out to be 40°C. In the case of green tea, the application of the entrainer did not noticeably influence the increase of the extraction's rate; however, it turned out that the entrainer, acting as the extract's solvent, facilitated its tapping and enabled conducting the process until the end. In both experiments similar final extraction outputs were obtained which equaled 2.95% for the temperature of 35°C and 3.08% for 40°C.

When increasing the scale it was decided to perform extraction at 40°C and to use ethanol as an entrainer with the additional function of extract solvent.

¼ technical scale

The reason behind performing extraction on a ¼ technical scale was the necessity to obtain higher amounts of extract for further application studies.

The process was carried out under a pressure of 25 MPa at temperatures determined as a result of laboratory trials. The extractions used an entrainer whose initial amount and flow during extraction constituted an increase of the laboratory scale and which resulted from the weight proportion of the used material. Results were presented of increasing the extraction scale of two portions of linseed cake and one portion of green tea leaves.

a) Linseed cakes

Two portions of linseed cake, initially oil-separated with cyclohexane, were subjected to extraction using supercritical CO₂. In the first portion, with a weight of 5.43 kg, the amount of oils marked using toluene extraction at boiling point equaled approx. 7% by weight, while in the second one, with a weight of 5.07 kg - approx. 6.5% by weight. Extraction using CO₂ was carried out at a temperature of 35°C and pressure of 25 MPa. One experiment used methanol as the entrainer, while the second one used ethanol. During extraction the entrainer was fed in a continuous way in the amount of 100 cm³/h. For the purpose of comparing the obtained data, the experiment results were converted into 5 kg of plant material feed, and the extract weight increments were related to the flow time of the same CO₂ volumes, equal to 1,180 dm³/h. The experiment results were presented below in Table 4.

Table 4

Experimental data for linseed cake (converted to 5 kg of material) - 1/4 technical scale

CO ₂ extraction with ethanol			CO ₂ extraction with methanol		
Time h	Cumulative amount of extract g	Cumulative extraction output %	Time h	Cumulative amount of extract g	Cumulative extraction output %
2	12.75	0.26	2.5	19.65	0.39
4	22.73	0.45	5	42.85	0.86
7	33.98	0.68	7.75	67.24	1.34
9	49.82	1.00	10.25	95.73	1.91
11	76.14	1.52	12.75	137.97	2.76
13	100.38	2.00	15.5	169.54	3.39
15	122.90	2.46	18	199.74	3.99
17	141.76	2.84	20.5	225.52	4.51
19	159.39	3.19	23	250.89	5.02
21	176.68	3.53	25.5	270.70	5.41
23	194.30	3.89	28.25	284.42	5.69
25	209.07	4.18	30.75	295.49	5.91
27	224.45	4.49	33.5	302.76	6.06
29	237.21	4.74	36	310.89	6.22
31	252.19	5.04	38.5	317.33	6.35
33	264.58	5.29	41	320.03	6.4
35	280.45	5.61			
37	295.25	5.91			
39	310.34	6.21			
41	323.68	6.47			
43	334.14	6.68			
45	341.17	6.82			
47	346.49	6.93			

A graphic representation of linseed cake extraction and the output of the process on a 1/4 technical scale was presented in Figure 4.

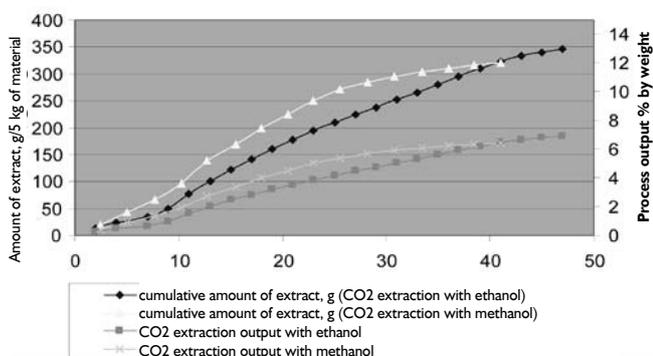


Fig. 4. Supercritical extraction for linseed cake – 1/4 technical scale

In both cases of extracting linseed cakes on a 1/4 technical scale using supercritical carbon dioxide, a complete separation of toluene-soluble elements was obtained at its boiling point. The differences in the final amount of extracts, and at the same time in the outputs of the process, resulted from an initial oil-separation of the cake portion before extraction.

Final outputs - 6.93% and 6.40% - turned out to be coherent with determining the amount of substances soluble in boiling toluene, in the material before extraction.

By comparing the extraction diagrams it may be seen that methanol is an entrainer for which the rate of extraction would be higher.

b) Green tea leaves

A portion of dried and ground green tea leaves weighing 4.7 kg was subjected to supercritical extraction using CO₂ and at a temperature of 40°C under a pressure of 25 MPa. Initially, 250 cm³ of ethanol was added to the material. During the process, the entrainer was fed in the amount of 100 cm³/h. The carbon dioxide flow equaled 650 dm³/h. The numeric results of the process were listed in Table 5.

Table 5

Experimental data for supercritical extraction of green tea leaves - 1/4 technical scale

Time h	Cumulative amount of extract g	Cumulative extraction output %
4	22.85	0.49
6	37.96	0.81
8	52.24	1.11
10	59.92	1.27
13.5	74.54	1.59
17.5	88.63	1.89
20.5	99.81	2.12
25	111.16	2.37
28	117.61	2.50
34	125.28	2.67
39.5	142.47	3.03
45.5	144.51	3.07
52	152.09	3.24
57	157.40	3.35
63.75	158.82	3.38
68.75	159.66	3.40

The increment of the extract amount was shown in Figure 5.

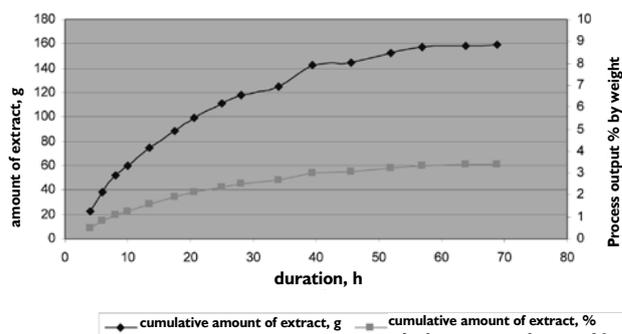


Fig. 5. Supercritical extraction of green tea leaves - 1/4 technical scale

During the extraction of dried green tea leaves on a 1/4 technical scale, the tapping of the extract was much more stable than on the laboratory scale. Larger piping diameters turned out to be less prone to blockage by the depositing extract. The final process output which equaled 3.4% was higher by 0.3% than the one obtained on a laboratory scale. The result could be caused by larger extract losses in case of its small amount.

Graphs of dried green tea leaves' extraction performed at a temperature of 40°C had a similar course for both process scales.

Summary

Extraction in supercritical conditions using CO₂ constitutes a useful technique of isolating elements from plant materials. The variety of materials and the differences of properties of the extracted elements resulting from this require a separate determination of process parameters for each case.

The presented examples pertained to the extraction of two significantly different plant materials (linseed cakes and green tea leaves) and extracts obtained from them. Linseed cakes, a residue of linseed after oil extruding, contain mainly oil, proteins and sterols. The obtained extract had the form of an oily liquid with a large viscosity. Dried green tea leaves contain flavonoids, polysaccharides, theine, caffeine and chlorophylls. During extraction the extract changes its form from waxy - semi-solid to solid.

The determination of the extraction's proper temperature and the confirmation of the relevance of using an entrainer, resulting from experiments conducted on a laboratory scale, was used when enlarging the scale.

Extraction results for the same materials were similar for both process scales. The course and times of extraction differed only slightly. In linseed cake extractions using an entrainer a total isolation of elements at boiling point was obtained, while the extraction process was favored by temperatures close to the critical temperature of CO₂ ($T_k = 31.05^\circ\text{C}$).

The course of processes and parameters determined as a result of trials on a laboratory scale turned out to be a helpful tool when enlarging the scale and were confirmed in extractions conducted on a 1/4 technical scale.

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