

Ultra high pressure supercritical carbon dioxide extraction and fractionation of plant materials

V. Steinhagen¹, Dr. C. Lütge¹, P. Kotnik³, Dr. Ž. Knez^{2,3}

¹Uhde High Pressure Technologies GmbH, Buschmühlenstr. 20, D-58093 Hagen, Germany,

²CINS d.o.o, Maribor, Slovenia,

³University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory for Separation Processes and product design, Smetanova 17, SI-2000 Maribor, Slovenia

Ultra high pressure extraction and fractionation of antioxidants from sage, rosemary and carotenoids containing plant material is presented. One of the main advantages of using SCF at ultra high pressure for extraction and fractionation of substances by stepwise reducing solvent power is demonstrated on very efficient concentration of valuable antioxidative compounds for the above mentioned materials.

The thermodynamic fundamental data for extraction and fractionation of sage antioxidative components were determined. Design of ultra high pressure equipment and economy of the processes will be given in presentation.

Key words: ultra high pressure, dense gases, ultra high pressure supercritical CO₂, extraction, plant materials

1. Introduction

Design of new products with special characteristics or design of new processes, which are environmental friendly and have an impact to sustainable processes, are a great challenge for chemical engineers. High pressure gave in several processes completely new products with special characteristics. Such new processes are environmental friendly, of low costs and sustainable.

Applying supercritical fluids for production of materials with unique properties and especially the legal limitations for solvent residues and restrictions on use of conventional organic solvents for isolation/fractionation of special components, increase the use of dense gases for extraction applications. On the other hand, fractionation of total extracts in combination with different formulation techniques, gives an additional impetus to the developments in the area of high pressure applications. Selective extraction of components or fractionation of total extracts is also possible by use of different gases for isolation/fractionation of components.

The limitation for further applications of this technique is the low solubility of several substances in carbon dioxide at elevated pressures (up to 500 bar) and consequently the extracts obtained by high pressure technologies are relatively expensive in comparison with conventionally obtained products. Due to the relatively low solubility of substances in this pressure range (up to 500 bar) cosolvents/entrainers are often added to the CO₂ to enhance the solubility. The disadvantage of using entrainers is the contamination of extracts with residues of the entrainer. Therefore, in this case expensive separation processes have to be applied for separation of the residual entrainer.

UHDE HPT executed ultra high pressure extraction tests with CO₂ as solvent for many different raw materials on a multipurpose extraction plant operating up to 2500 bar and

exploited the most important advantage of using supercritical fluids at ultra high pressure - selective extraction of components or fractionation of total extracts [1-4].

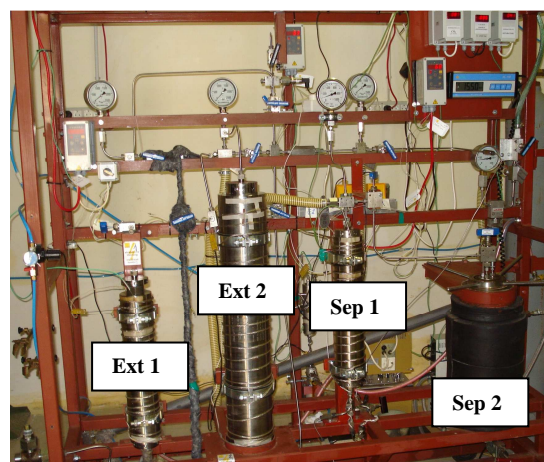
Because the solubility of several dense gas low soluble substances increases with increasing pressure and temperature ultra high pressure (up to 2500 bar) enables an economic feasible extraction of substances from plant materials. Direct multi-stage fractionation of substances from the extract by pressure and/or temperature dependant precipitation is a cost advantage of these processes.

Some patent applications could be found where higher pressure is used for separation of substances from plant materials at pressure up to 1000 bar. Although most of industrial units for caffeine separation are operating at up to 350 bar, in a patent [6] separation of caffeine from tea is described at pressure up to 1000 bar and temperature up to 80°C. Isolation of xanthohumol rich hop extracts at 60 °C and high pressure is described in other patents [7].

For industrial applications pressures higher than 500 bar were unusual in the past and most of the industrial high pressure plants using supercritical CO₂ operate at pressure from 300 bar to 500 bar. Current new extraction units are operating up to 700 bar or even at 1000 bar.

This presentation will show one of the main advantages of using SCF at ultra high pressure for extraction and fractionation of substances that by stepwise reducing solvent power extended fractionation of extracts could be obtained. Fundamental data for separation of sage components and examples on multi step separation of components from sage, rosemary and carotenoids containing plant material will be given.

2. Ultra high pressure extraction equipment with 2 separators



	Parameter
Extractor 1	Volume: 0.64L Maximal operating pressure: 2800 bar Maximal operating temperature: 90°C
Extractor 2	Volume: 2.0L Maximal operating pressure: 2800 bar Maximal operating temperature: 90°C
Separator 1	Volume: 0.64L Maximal operating pressure: 2800 bar Maximal operating temperature: 90°C
Separator 2	Volume: 1.0L Maximal operating pressure: 1000 bar Maximal operating temperature: 120°C
Flow rate of CO ₂	Max 16 kg CO ₂ /h

Figure 1: Ultra high pressure extraction unit and technical characteristics

In this apparatus the direction of flow of the supercritical solvent through the fixed bed can be upwards or downwards.

3. Examples

3.1. Sage

Ultra high pressure CO₂ extraction experiments

Total yield for isolation of carnosolic acid, carnosol and other components from sage extracted at pressures 700 bar and 1300 bar, extraction temperatures 60°C, 80°C and 100°C and S/F 20, 40 and 60 kg CO₂ per kg feed amounted to 9.95 wt% to 17.63 wt%; calculated on dry mass on sage the yields were from 3.93 wt% up to 8.61 wt%.

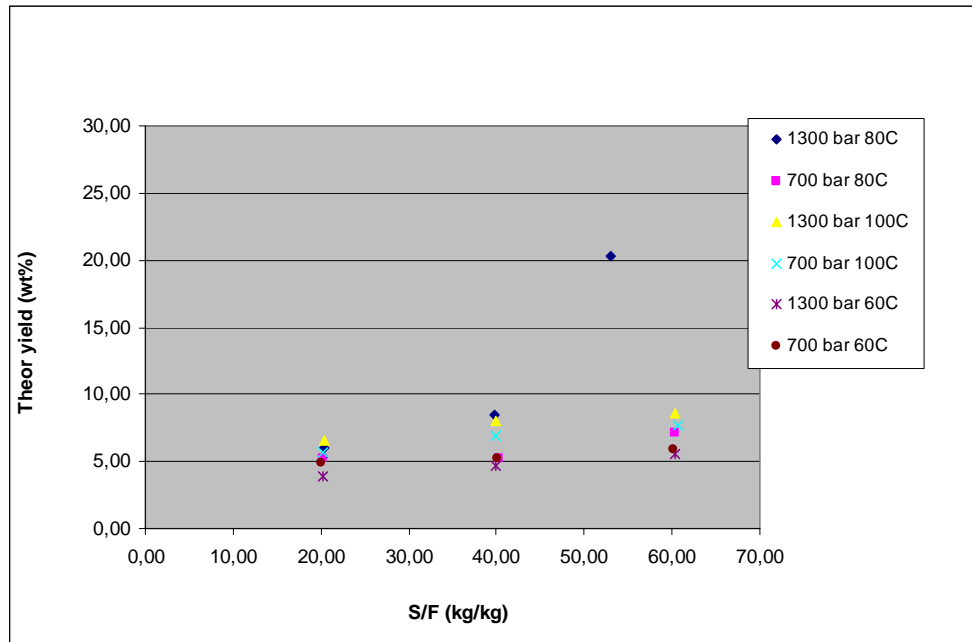


Figure 2: Theoretical yield vs. S/F on dry material

Influence of pressure on yield

At constant temperature 60°C, 80°C and 100°C the total extraction yields increases with increasing pressure at constant ratio S/F ($m_{\text{CO}_2}/m_{\text{feed}}$). The content of carnosolic acid and carnosol in extracted sage material (raffinate) decreases with increasing extraction pressure at constant extraction temperature and constant S/F.

Influence of extraction temperature on yield

Extraction experiments were performed at temperatures 60°C, 80°C and 100°C and it is evident that the extraction temperature has a high impact on the total extraction yield, degree of extraction of carnosolic acid and of carnosol at constant pressure and constant S/F.

At constant pressure of 1300 bar an increase of the total extraction yield with increasing temperature at constant S/F could be observed. Degree of extraction of total present carnosolic acid is very much influenced by the temperature. In extraction experiments at pressure 1300 bar the highest degree of extraction (98.66%) of carnosolic acid could be observed at 100°C. At lower extraction temperature the degree of extraction of carnosolic acid was between 79.40% and 88.38%.

Influence of S/F on yield

Total extraction yield increases with increasing S/F ($m_{\text{CO}_2}/m_{\text{feed}}$) at constant extraction pressure at constant extraction temperature. The highest total extraction yield was obtained at a pressure of 1300 bar and an extraction temperature of 100 °C and a S/F of 60.

The degree of extraction of carnosolic acid is very much dependant on extraction pressure and extraction temperature, but again the higher S/F gave higher degree of extraction. The same phenomenon was observed for isolation of carnosol from sage where degree of extraction of carnosol is very much dependant on extraction pressure and extraction temperature and higher S/F gave higher degree of extraction.

Phase observations for the system sage extract/CO₂

Phase observations were made at 23°C, 40°C, 60°C, 80°C and 98°C in pressure range from 20 to 590 bar and some pictures are presented on figure 3.

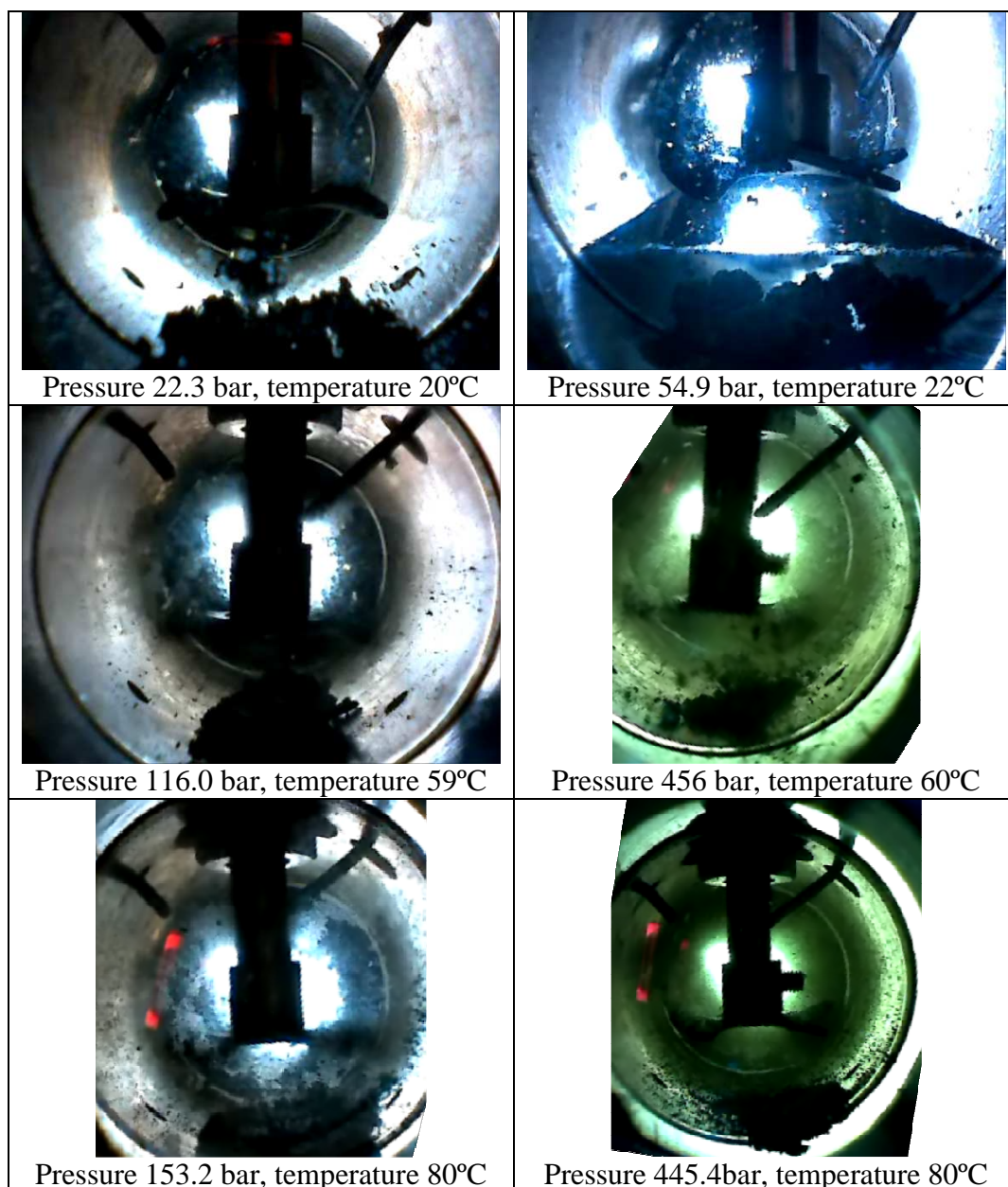


Figure 3: Phase behavior of sage extract/CO₂ at various pressures and temperatures

Solubility determination of sage extract in CO₂

Solubility of substances from sage extract increases with increasing pressure at constant temperature. The solubility also increases with increasing temperature at constant pressure. Based on measured data and phase observation it was predicted that pressure in separator S1 should be between 150 bar and 250 bar, while the temperature should be between 40°C and 80°C.

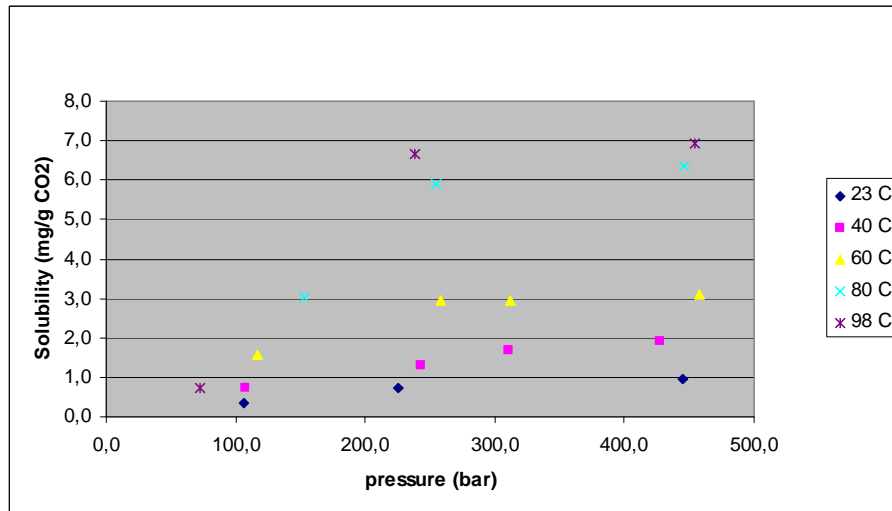


Figure 4: Solubility of sage extract in CO₂ vs. pressure and temperature

Multi-stage separation of sage extract

Till now no study on fractionated separation of sage extracts produced with UHP CO₂ extraction have been published.

In a multi-step separation, pressure and temperature in first separator have a high influence on the yield and composition of the product in separator S1 and subsequently in separator S2.

In two-stage separation experiments part of the extract mass were collected in separator S1 and the other part in separator S2. Separator S1 was operating at pressures 150 bar and 250 bar and temperatures 40°C, 60°C and 80°C. In single-stage separation experiments, separation of extract from CO₂ was performed in separator S2. Separator S2 was always operating (in single-stage and in two-stage separation experiments) at a pressure of 20 bar and a temperature of 19-20°C.

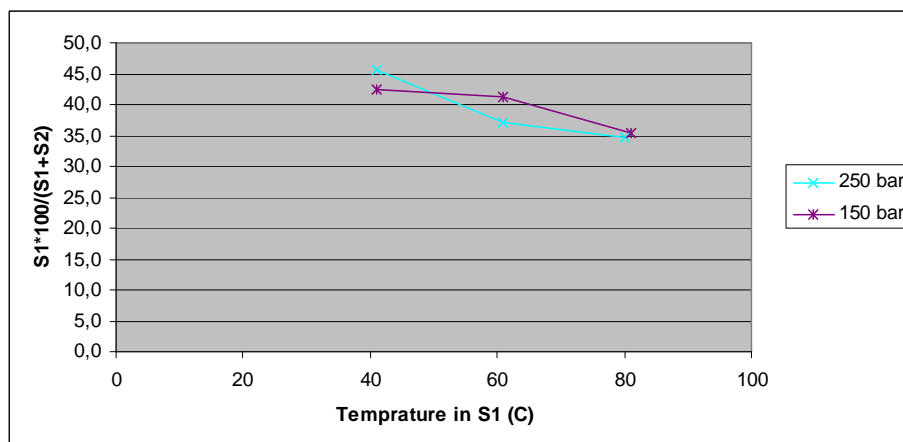


Figure 5: Ratio of mass vs. pressure and temperature in separator S1

For the composition of the extracts from experiments where temperature in separator S1 was 41°C it is evident that the concentration of carnosolic acid in separator S1 was higher than the concentration of carnosolic acid obtained in single stage separation experiment at pressure 250 bar in S1. The content of carnosolic acid in extract separated in S1 at pressure 150 bar and temperature 41°C was only 9.57 wt% what is lower than in the extract obtained in single stage separation experiment performed at same extraction process conditions (13.50 wt%).

At a temperature of 61°C and operating pressure of 150 bar and 250 bar in S1 the concentration of carnosolic acid in obtained extract in S1 separator pressure 250 bar as well as at 150 bar were lower than in single-stage separation experiments.

At temperature 80°C in S1, the concentration of carnosolic acid was 18.12wt% at pressure 250 bar, while at 150 bar extremely good separation efficiency was obtained and the concentration of carnosolic acid in the extract was 22.42 wt%. This concentration of carnosolic acid is as high as in industrial products which are used as commercial antioxidant in food products.

3.2. Rosemary

Total yield for isolation of carnosolic acid, carnosol and other components from rosemary extracted at pressures 1000 bar and 1500 bar, extraction temperature 80°C, S/F 20, 40 and 60kg CO₂ per kg feed and were from 14.10 to 18.53 wt%.

During extraction process water was co-extracted. Content of water in extraction residues decreases with increasing extraction pressure and increasing S/F. The residual water content in extraction residues, extracted at various process conditions varied between 1.28 wt% and 3.95 wt%, while in the extracts water content was between 12.20 wt% and 50.93 wt%. Water from the extracts could not be easily separated therefore the results are given on the composition of extracts as such.

For industrial application of extracts of rosemary content of carnosolic acid in the extract has to be high, but the concentration of essential oil has to be relatively low.

Therefore fractionated separation was studied and the results gave excellent separation of carnosolic acid and aromatic components. At certain process conditions in separators S1 and S2 the enrichment on carnosolic concentration of more than 10 was obtained. The aromatic components were practically quantitatively separated in low pressure separator.

In experiments on fractionated separation of rosemary extracts produced with ultra high pressure CO₂ extraction separator S1 was operating at pressures 100 bar, 200 bar and 300 bar and temperatures 40°C and 60°C. In single-stage separation of extract from CO₂ was performed in separator S2. Separator S2 was always operating at pressure 50 bar and temperature 40°C.

As could be seen from data in Figs. 6 and 7, higher pressure in S1 at temperature 40°C gave lower mass fraction of total extract in S1. This mean that at higher pressure more products are collected in separator S2.

At temperature 40°C and pressure 200 bar in separator S1 the maximal concentration of carnosolic acid was found. The highest concentration of carnosolic acid (21.49 wt%) in was in separator S1 operated at temperature 40°C and pressure 200 bar, while the extraction was performed at pressure 1000 bar, extraction temperature 80°C and S/F 40 kg/kg. The extract in separator S2 contain at this process conditions 9.61 wt% carnosolic acid. The maximum mass fraction and mass fraction of total carnosolic acid in separator S1 was at temperature 40°C and pressure in separator 100 bar while the extraction was performed at pressure 1000 bar, extraction temperature 80°C and S/F 40 kg/kg. In this case in S1 also other substances were

precipitated and therefore the concentration of carnosolic acid in extract were lower (15.80 wt%).

At temperature 60°C in separator S1 higher pressure gave lower mass fraction of total extract in S1. The concentration of carnosolic acid in extracts decreases with increasing pressure in S1. The highest concentration of carnosolic acid (22.04 wt%) was obtained in separator S1 operated at temperature 60°C and pressure 100 bar, while the extraction was performed at pressure 1000 bar, extraction temperature 80°C and S/F 20 kg/kg. The extract in separator S2 contain at this process conditions only 1.84 wt% of carnosolic acid.

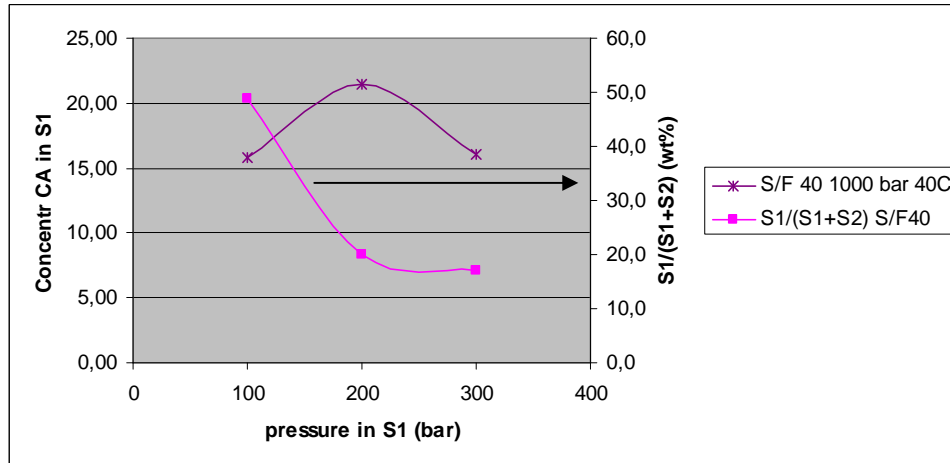


Figure 6: Concentration of carnosolic acid and ratio of total mass in S1 at separator temperature 40°C vs. separator S1 pressure

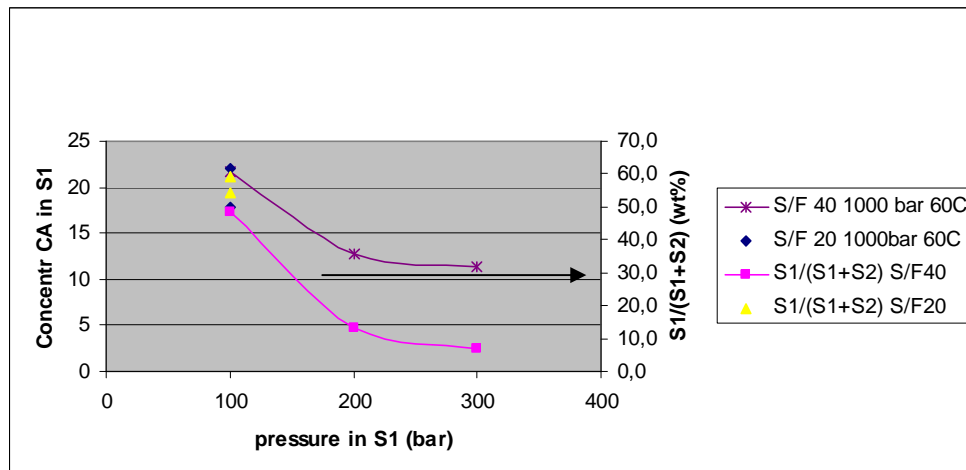


Figure 7: Concentration of carnosolic acid and ratio of total mass in S1 at separator temperature 60°C vs. separator S1 pressure

3.3. Carotenoid extracts fractionation

Isolation of carotenoids from plant materials at pressures below 400 bar is practically impossible without use of entrainers. At pressures higher than 700 bar the solubility of carotenoids is good enough that relatively low ratios S/F (m_{CO_2}/m_{feed}) could be used for the extraction of carotenoids.

Plant materials were extracted at ultra high pressure and fractionated separation gave extracts with high concentration of carotenoids.

Based on phase equilibrium data, separation conditions for operation of separator S1 were determined. Extraction experiments were performed in a pressure range of 700 bar up to 1500 bar at temperatures 40°C and 60°C.

Results of fractionated separation are presented in table 1.

Table 1: Influence of multi-stage separation procedure on carotenoids concentration in extract (extraction was performed at 1500 bar and 60°C, S/F=40) and mass ratio of total extract in separators S1 and S2 and concentration of carotenoids in fractionated extracts

P in S1 (bar)	wt % of extract in S1	Concentration of carotenoids in extr. in S1 (mg/kg)	Wt % of extract in S2	Concentration of carotenoids in extr. In S2 (mg/kg)
300	21.80	3320	78.20	1930
250	35.57	3772	64.43	1612
200	47.99	4620	52.01	551

Temperature in S1 was 60°C, pressure in S2 was 50 bar temperature was 50°C

4. Conclusions

One of the major advantages of SC fluid extraction processes performed at ultra high pressure fractionation of extracts decreasing the solvent power of CO₂ is presented. Antioxidative compounds from sage rosemary and carotenoid containing material were very efficiently fractionated by two step separation.

For the design of separation process for fractionation of sage extract components fundamental thermodynamic data were determined.

The possible limitation of SCF technologies could be in high investment costs, but the legal restrictions on solvents and solvent residues, fractionation of highly valuable compounds from total extracts in combination with formulation processes will lead to an increase in the use of gasses under high pressure for extraction applications.

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