Effect Of CO_2 Pre-Treatment On $scCO_2$ Extraction Of Natural Material

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In order to enable an efficient extraction, an adequate pre-treatment of the natural source material is essential. Usually, plant material is at least pre-treated by means of mechanical methods such as milling, flaking or pelletizing.
In this study, in addition to common mechanical pre-treatment the solvent CO_2 was used for further conditioning the material. For this purpose, different kinds of solid substrates like oilseeds and herbaceous material were subjected to a depressurization after a certain contact time with CO_2 at elevated pressures.
This treatment was performed either prior to extraction or during the extraction process when the plant material is already partly extracted. It was noticed in extraction kinetics obtained with $scCO_2$ that extraction of several classes of natural material can possibly be improved by such conditioning induced by decompression. Decompression may cause cracks in the cell structure of the plant matrix.
With the purpose to gain a better understanding of the mechanisms occurring during CO_2 conditioning, experiments were carried out in a high pressure magnetic balance. In this way, the time-course of CO_2 dissolving into the plant material during compression as well the reverse process during decompression was determined.

INTRODUCTION

Extracts from plants have various applications in food, cosmetic and pharmaceutical industry.
For production of natural extracts from plant material organic solvents like alcohols or other hydrocarbons can be used. Alternatively, compressed gases such as supercritical (sc) CO_2 play an important role especially when high quality extracts with high purity and low contaminations with solvent residues are demanded.
Prior to production of extracts from natural material, the solid substrates are usually processed by mechanical and/or thermal methods to prepare the material for a subsequent efficient extraction. The main aim of the pre-treatment is to release the solute inside the solid in order to permit good accessibility for the solvent. As a side effect, pre-treatment is usually accompanied by fracture of the solid substrate.
In this study, the decompression treatment is investigated as an alternative conditioning method. Therefore, natural material is brought in contact with CO_2 at elevated pressure and temperature and after certain holding time it is decompressed rapidly.
In a previous work, the effect of this type of pre-treatment on subsequent extraction had been investigated for ginger and valerian roots as well as plants of the *Lamiaceae* species. Those

types of plant material showed significant swelling in a compressed CO_2 atmosphere either during the pressurization or decompression step [1].
In this study, the underlying mechanisms of this conditioning method were investigated. For this purpose, sorption and desorption behaviour was determined gravimetrically in a magnetic suspension balance.
In literature, various works reported that considerable amounts of CO_2 dissolve within oily liquids. Thus, a possible mechanism occurring during contacting natural material with CO_2 at elevated pressure is expected to be the dissolution of the gas within the solute phase in the material.
For this reason, different kinds of natural material were chosen. On the one hand, the oil seeds rape and sunflower were investigated because they contain a relatively high amount of extractables in which CO_2 may dissolve. On the other hand, herbaceous St. Johns Wort with a ten-fold lower content of extractables was studied.
The main goal of the study is to obtain better understanding on the actions taking place during pressurizing and decompression of natural material. The observations presented are joint results from the two institutes.

MATERIALS AND METHODS

Plant Material

Rapeseed originated from LHG eG Schmölln, a German agricultural trade association. Dehulled sunflower seeds destined for end-use were purchased from a local supplier. Moisture content was determined by drying at 103 °C for 16h at 5.6 and 3.9 %, respectively. Oil content was determined by Soxhlet extraction with hexane according to official DGF method resulting in 45 % for rapeseed and 49 % for sunflower seed.
St. Johns Wort was cultivated in southern Serbia. Hop pellets (Magnum) originated from Fertilizers Research Institute, Pulawy, Poland. Moisture content determined by Karl-Fischer titration was 9.6 % and 11.2 %, respectively. Content of extractables determined by Soxhlet extraction with hexane was approximately 3 % for St. Johns Wort and 23 % for hop pellets.

Mechanical pre-treatment

In order to test mechanical pre-treatments with different efficiency, the plant material was either manually cut with scissors (St. Johns Wort) or ground in different kinds of mills.
A roller mill (Comet, Germany) was used to produce flakes of plant material. The gap width between the counter-rotating rollers (D = 60mm, 144 rpm) was 0.15mm. One roller had a plane surface; the other was riffled in order to ensure proper feeding of solids.
An ultra-centrifugal mill of the type ZM200 (Retsch GmbH, Germany) equipped with a 12-teeth rotor was used to impact-mill the material. Optionally, the ZM200 can be operated with a circular static sieve with a mesh width of 1mm surrounding the rotor. In this case, in addition to fracture by impact shear stress is applied on the material and grinding efficiency is increased.

Carbon dioxide

Technical grade CO_2 of 99.95 % (Westfalen Gase, Germany) purity was used for lab scale experiments. For pilot scale extractions CO_2 had a purity of 99.5% (Yara GmbH, Germany).

Sorption of CO_2 into natural material

Sorption kinetics were determined gravimetrically by means of a magnetic suspension balance (Rubotherm, Germany) connected to a high pressure cell placed in an isothermal environment. The experimental setup is similar to that used in a previous work [1]. Sample material is connected inside the pressure cell with a permanent magnet whose vertical position is kept constant by a controller that regulates an electromagnet. Weight changes of the sample are detected by the corrective actions of the controller that are necessary to maintain the position of the permanent magnet. Evaluation of the acquired data and conversion into weight changes is achieved on-line by control software of a PC.

The resulting weight changes of the sample observed during the sorption experiment is a superposition of weight increase due to sorption of the dense gas into the natural material, weight loss due to extraction of components by the surrounding gas acting as solvent and changes of buoyancy caused by potential volume change (swelling) of the plant material.

The kinetics is recorded as the weight changes of the sample after pressurization with CO_2; desorption kinetics was determined subsequent to the sorption experiment after depressurization of the cell down to atmospheric conditions and measuring the mass change of the sample.

Extraction with $scCO_2$

Extractions were carried out on laboratory and pilot scale. On laboratory scale, experiments were performed with the Autoclave Engineers Screening System. Details on the setup were previously published [1]. Temperatures and pressures tested were in the range of 40-50 °C and 12 to 29 MPa, respectively. In this experimental set-up extraction is run as a one-pass process of the solvent; CO_2 is fed at flow rates of 0.3 – 0.5 kg/h to the extraction vessel (V = 150mL) where mass transfer takes place. After leaving the extractor, the loaded CO_2 is depressurized and enters the separator vessel where the extract is precipitated. Subsequently, CO_2 is released to the atmosphere.

The extraction plant on pilot scale is a closed cycle extraction plant. The volume of the extraction vessel amounts for 1.3 L. Solvent circulation is driven by a high pressure piston pump allowing mass flow rates of solvent of up to 20 kg/h. After extraction the solvent CO_2 is regenerated by decompression down to 6 – 7 MPa.

Decompression treatment

Decompression treatment of plant material was performed in the respective extraction vessel of the $scCO_2$ extraction plant on laboratory or pilot scale.

After a designated holding time at conditions similar to those applied in the respective extraction run the vessel loaded with plant material was depressurized.

RESULTS

Effect of decompression on $scCO_2$ extraction

An effect of decompression treatment on extraction yield was most evident for St. Johns Wort. Results for $scCO_2$ extractions of milled St. Johns Wort are shown in fig. 1. Extraction kinetic is represented as extraction yield as a function of specific cumulative CO_2 mass consumed. In the experiment with decompression treatment plant material was exposed for 1h

to CO_2 at P=12 MPa and T=40°C and subsequently decompressed down to atmospheric conditions before CO_2 flow was started.
It can be seen that the yield obtained in the experiment with decompression treatment amounts to about 2.9 % in comparison to 2.2 % obtained in the experiment without decompression prior to the extraction. At the beginning of the apparently process a higher extraction yield occurs due to the fact that during 1h exposure of the plant material mass transfer of compounds to the CO_2 occurs and these compounds are collected in the separator during the decompression. On the contrary, similar slopes of the extraction curves apart from the first data point of the extraction after decompression treatment are evident. This indicates that the operational loading of CO_2 with solute was similar for both experiments and means that the extraction rate was not influenced significantly by the decompression treatment. However, due to the plant tissue cracking caused by the rapid decompression, there is a higher availability of the extractables remained in plant tissue to supercritical fluid which enabled higher extraction yield (2.9%) which was not possible to obtain in the process without decompression (2.3%).

This is a difference to observations made for valerian root [2], where much faster extraction rates were found after decompression of the material. However, in case of valerian root obvious swelling with a volume increase of up to 50 % were found. For St Johns Wort, swelling did not occur and for this reason extraction rates were not increased because diffusion within the material was not improved by decompression.

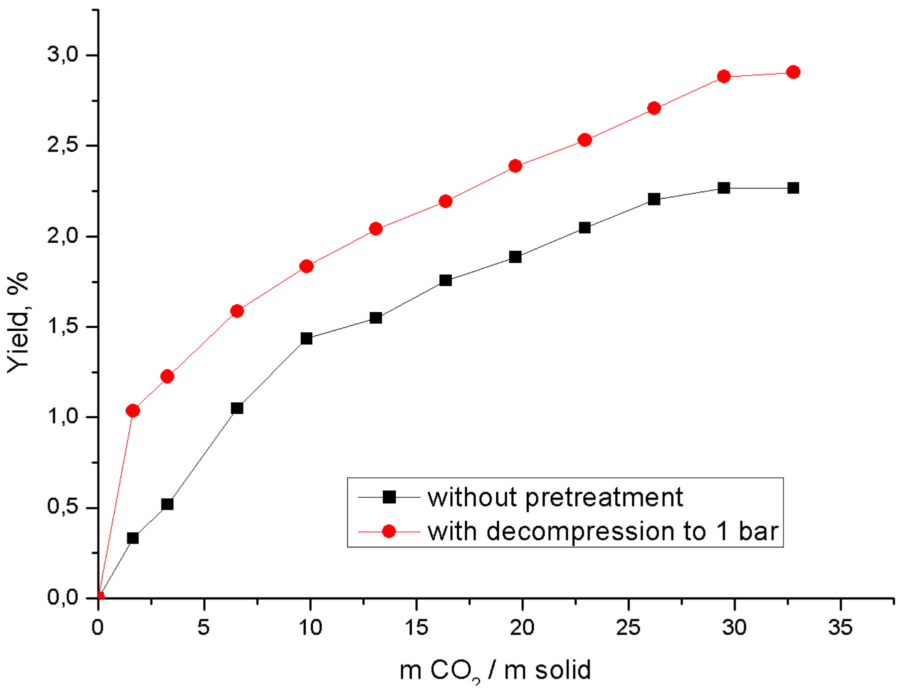

Figure 1: $scCO_2$ extraction of St. Johns Wort at 12 MPa and 40 °C. $\dot{m}_{CO2}$ = 0.5 kg/h. Laboratory scale, decompression prior to extraction.

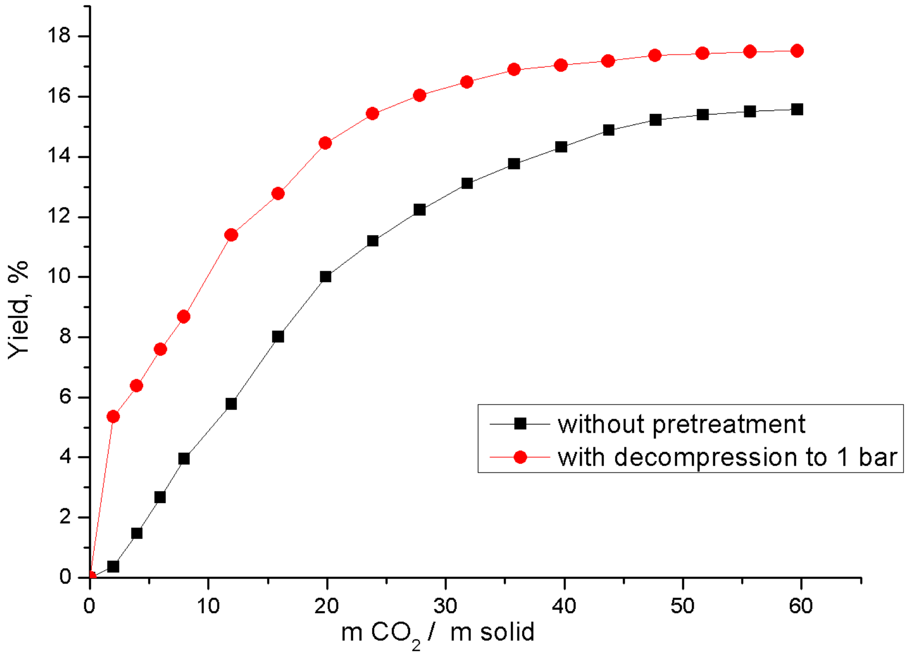

Figure 2: $scCO_2$ extraction of hop pellets at 29 MPa and 50 °C. Laboratory scale, $\dot{m}_{CO2}$ = 0.3 kg/h, decompression prior to extraction

Similar observations were made for hop pellets with respect to the increase of yield after a decompression treatment. As for St. Johns Wort the extraction rate was not increased for this material probably due to the lack of swelling caused by decompression (fig. 2).
In addition to decompression treatment prior to extraction this type of treatment was also performed in the course of the extraction process. A positive effect on extraction yield was observed as well.

On pilot scale, the effect of decompression on extraction was studied during the course of extraction.
Exemplarily the effect of decompression of rapeseed is shown in fig. 3. Mechanical pre-treatment prior to extraction was impact-milling. The point of time when decompression was performed is marked by arrows.

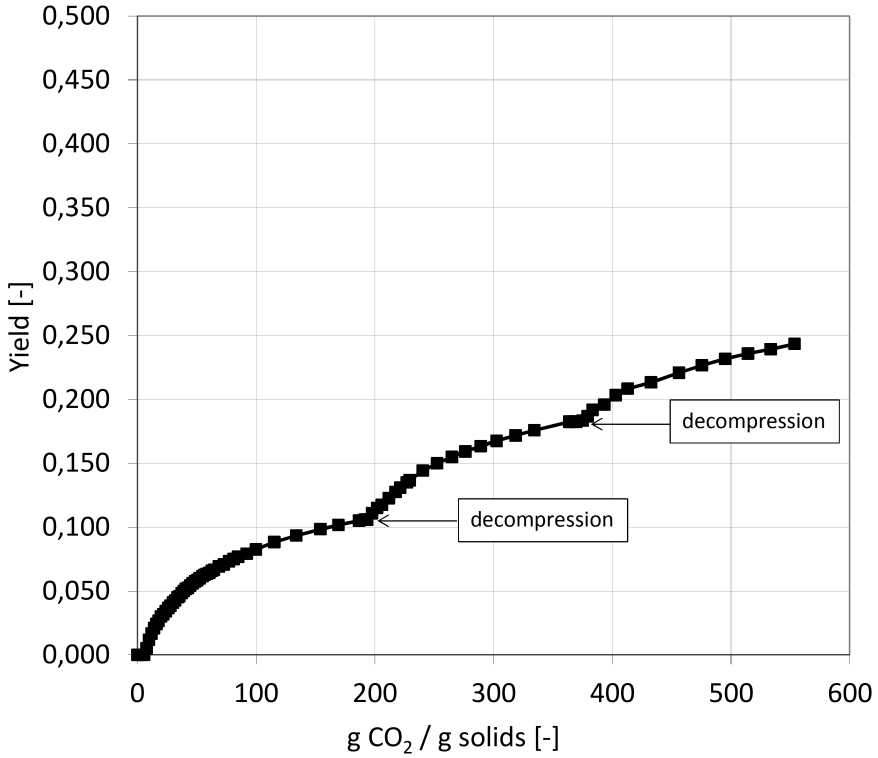

Figure 3: scCO_2 extraction of flaked rapeseed at 30 MPa and 60 °C. Pilot scale, $\dot{m}_{CO2}$ ≈13 kg/h. Decompression prior to extraction

In fig. 3, an increased extraction rate after each decompression can be seen. However, in case of rapeseed the effect on the extraction rate tends to be more distinct when a longer period of time elapses between decompression and re-extraction. For this reason it must be concluded that homogenization of the oil within the particles takes place and thus shorter diffusion pathways through the particles are the reason for the improved extraction rate after decompression.

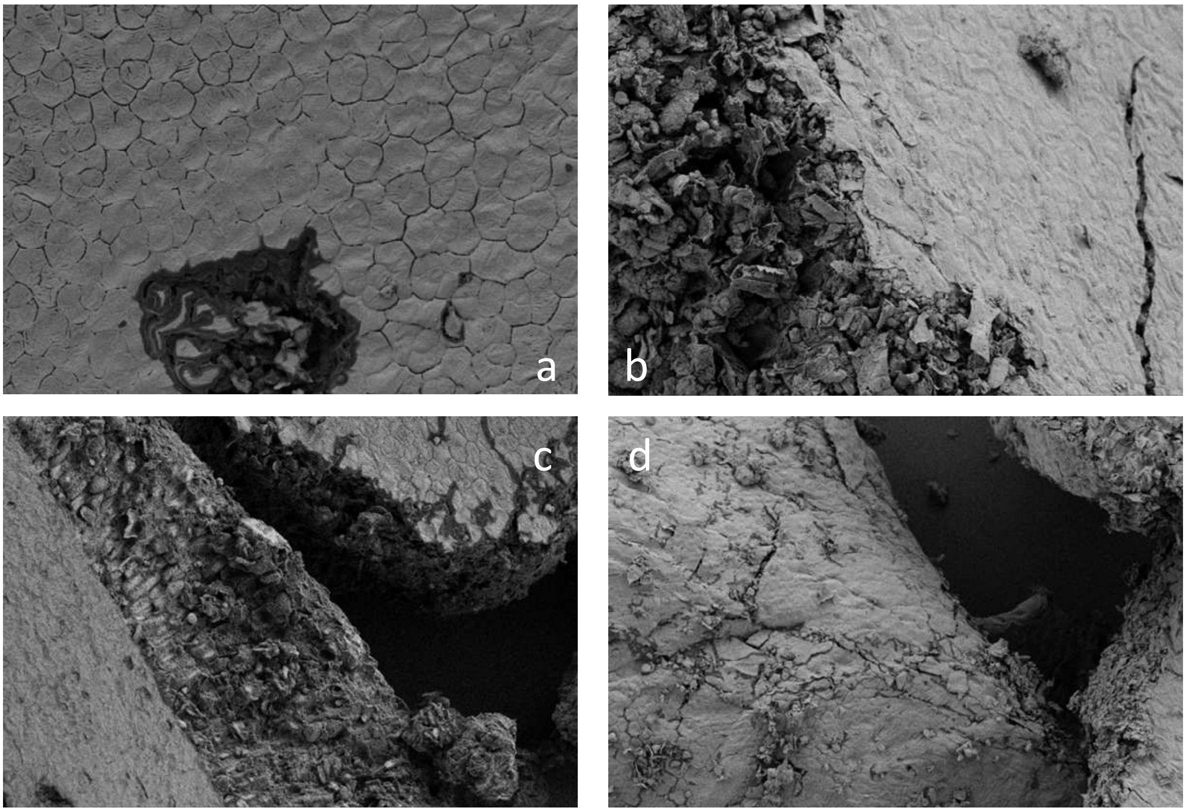

Figure 4: a) 1000x impact-milled rapeseed b) impact-milled rapeseed after CO_2 extraction and decompression c) milled rapeseed (impact+shear) d) milled rapeseed (impact+shear) after CO_2 extraction and decompression

On the other hand, a destructive effect is observed in material that was exposed to CO_2 and decompressed. In fig. 4, SEM images of milled rapeseed are presented. The material that was exposed to CO_2 shows additional crackings propagating along the cell walls of the plant matrix.

In tab. 1, an overview of the experiments of scCO_2 extraction with decompression treatment is shown.

Table 1: Overview of the experiments on the effect of pre-treatment on extraction

Material	Scale	mechanical pre-treatment	Extraction conditions		effect of decompression on extraction yield	
			P [MPa]	**T [°C]**	**prior to extraction**	**in the course of extraction**
hop	laboratory	pelletizing	29	50	++	+
St. Johns Wort	laboratory	cutting	12	40	+++	+++
		milling	12	40	++	
Rapeseed	pilot	impact-milling	30	60		++
		flaking	30	60		+/o
Sunflower seed	pilot	impact-milling				+/o
hop	pilot	pelletizing	29	50		+
St. Johns Wort	pilot	impact-milling	12	40		++

Sorption of CO_2 within plant material

In order to achieve better understanding on the mechanisms underlying the effect of decompression of natural material, the sorption behaviour of CO_2 within the different natural materials was studied.

In figure 4, a typical sorption-desorption-sequence is shown for the example of sunflower seed at P = 15 MPa and T = 60 °C. Desorption is displayed as positive weight change. This permits the direct comparison of the two processes with respect to equilibrium loading of the natural material with CO_2 and rates of sorption and desorption.

It can be seen that the desorption proceeds faster than the sorption. This was observed for all tested materials. In case of sunflower seed the explanation is quite obvious because material was pulverized by decompression. However, a faster desorption was observed for the other investigated materials as well although the change of the macroscopic structure was less obvious. In case of rapeseed, broken hulls were observed whereas the shape of St. Johns Wort appeared to be unchanged after the experiment.

Furthermore, a difference between loading of plant material with CO_2 in sorption and desorption experiments can be seen.

Such a discrepancy between of amount sorbed and desorbed was observed throughout the experiments. This demonstrates that the results underlie an uncertainty that is based on various effects as explained in the following.

On the one hand, during the time of pressurization and decompression, buoyancy changes continuously until the pressure and temperature is constant. This influences the recorded weight of the sample and complicates identification of the starting point of sorption because the signal acquired by the balance is a superposition of buoyancy, gravitational and bearing force.

In addition, extraction of compounds from the natural material to the surrounding dense gas atmosphere occurs leading to a decrease of the net weight of the sample.

In order to keep extraction effects low, mainly mechanically untreated materials were used. In tab. 2, an overview of the sorption experiments carried out in this study is summarized. For the reasons explained above, mean values obtained from sorption and desorption experiments are shown.

In all but one case CO_2 loading of the material is higher for increasing pressures. This reveals a certain consistency of the results.

Furthermore, as a trend, more CO_2 is sorbed in sunflower seeds when compared to rapeseed although both materials are oilseeds with comparable composition. It was expected that especially the oil content plays an important role for sorption of CO_2 within natural material. In literature, various authors report a considerable dissolution of CO_2 within oily phases of more than 30 wt. % at tested conditions [3],[4].

However, results of sorption on St. Johns Wort show a different trend. Although data for St. Johns Wort are somewhat contradictory with respect to the influence of pressure, in general, sorption of CO_2 within this herbaceous material tends to be higher. This was not expected when assuming that sorption takes place mainly as dissolution within the liquid phase inside the solids.

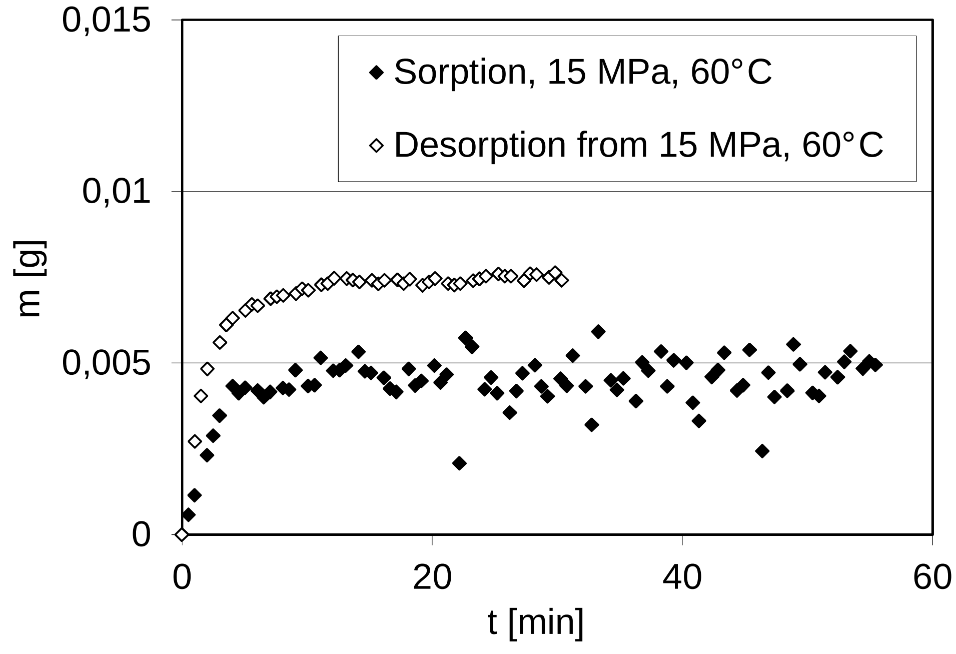

Figure. 4: Sorption and desorption kinetics of CO_2. Plant material: sunflower seeds. Conditions: 15 MPa and 60 °C.

Table 2: results for sorption of CO_2 within various natural material

Material	T [° C]	P [MPa]	gas loading# [wt. %]
Sunflower seed (unhusked)	60	15	3.35
	60	25.5	7.44
Rapeseed (husked) - whole grains	60	15	2.87
	60	26	3.35
- deoiled, (desolventized extraction residue from Soxhlet extraction)	60	5	2.18
	60	15	5.84
St. Johns Wort (cut)	40	15	11.88
	40	26	9.20

mean value obtain from sorption and desorption

CONCLUSION

The effect of decompression treatment after exposure to dense CO_2 was investigated for different kinds of natural material. The most obvious macroscopic effect of decompression was observed for sunflower seeds such as a pulverization of the material occurred. In case of rapeseed fracture of the material was less pronounced although cracking of the hulls was also observed.

In contrast, almost no change of macroscopic shape was observed for St. Johns Wort although the positive effect of such treatment on extraction yield was most distinct for this material. In this case, an increase of the final extraction yield was about 30 % after decompression treatment.

In order to investigate the fundamentals of decompression treatment, sorption and desorption behaviour was determined. It was expected that dissolution of CO_2 within the solute phase of the natural material is the predominant action taking place during sorption of CO_2.

However, sorption on St. Johns Wort tended to be higher in comparison to sorption in oilseeds although the content of extractable compounds in which CO_2 may dissolve is significantly lower than in case of oilseeds.
For this reason, in addition to dissolution of CO_2 within the liquid phase inside the natural material adsorption phenomena on the plant matrix may play an important role in the sorption of CO_2 within natural material.

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