

GREEN PROCESSING USING ALTERNATIVE SUPERCRITICAL FLUIDS FOR LOWER ENERGY CONSUMPTION

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ABSTRACT

Chemical and biochemical processes are mostly performed in solutions. Separation processes and product formulation require the use of solvents or of high temperature in processing steps. Conventional solvents are potential environmental pollutants, and the application of heat involves high energy consumption; therefore research is oriented towards the development of new processes with lower environmental impact. High pressure technologies involving sub and supercritical fluids offer the possibility to obtain new products with special characteristics or to design new processes, which are environmentally friendly and sustainable. By using high pressure as a processing tool one can also avoid the legal limitations for solvent residues and restrictions on use of conventional solvents in chemical processes. Supercritical fluids are already applied in several processes developed to commercial scale in pharmaceutical, food and textile industries. Extraction of valuable compounds from plant materials and their “in situ” formulation in products with specific properties is one of the very promising applications of high pressure technology. Particle formation using supercritical fluids may overcome the drawbacks of conventional particle size reduction processes. Because of their unique thermodynamic and fluid-dynamic properties, dense gases can also be used for impregnation of solid particles and particle coating. Use of alternative supercritical fluids for processing of different substances will be presented. Phase equilibria as a basis for design of micronisation, extraction processes using propane and argon in comparison to carbon dioxide will be presented. An overview on some applications and future expected development in the field of sub and supercritical fluids will be presented.

Keywords: supercritical fluids, extraction, micronisation, argon, propane, carbon dioxide.

INTRODUCTION

High pressure technologies involving sub- and supercritical fluids as solvents in order to develop sustainable processes involve also investigation of non-conventional supercritical fluids as a working tool and noble gases have many properties that make them a good candidate to be taken into consideration especially when presence of oxygen could be dangerous or harmful for component and therefore an inert solvent is essential. The most reasonable choice in that case is argon as the third most common gas in Earth's atmosphere (0.93 %) by volume with very low thermal conductivity and an inert nature. Its critical point ($T_c = -122.46$ °C, $P_c = 48.63$ bar) can be accessed easily [1]. It is already widely applied in food industry as a protective atmosphere for certain foodstuffs, notably fruits and vegetables,

especially when deterioration of food should be slowed down [2]. There are several chemical processes as extraction, micronisation, chemical and biochemical reaction which use supercritical fluids as solvents. For scale up design of the supercritical fluid processes solubility data are significant process parameters. There is a lack of data in the literature regarding the comparison between using supercritical carbon dioxide and subcritical propane focusing to solubility or phase equilibrium data of different compounds.

Phase equilibrium of argon with vanillin as the principal flavor and aroma compound in vanilla is taken under investigation even if vanillin alone does not characterize the vanilla flavor. Due to the relative shortage of supply of natural extracts of vanillin artificial vanilla flavoring is often a solution. Consequently, the development of new sources of vanillin, which are mainly biotechnologically oriented [3, 4, and 5] has been encouraged. Ethyl vanillin is used as an alternative to vanillin and the flavour and odour is approximately three times as potent as vanillin [5]. Data concerning phase equilibria of vanillins in a non-conventional SCF (like argon) has not been yet reported.

MATERIALS AND METHODS

Materials

Preparation of material

Particle size distribution and Analysis of water content in plant material were performed for the ground vanilla pods. Medium particle size is 0.62 mm and the moisture content of 7.9 % was determined gravimetrically by means of Mettler Toledo HB43-S Compact Halogen Moisture Analyzer.

Apparatuses

High pressure view cells

Prior to extraction experiments solubility measurements were performed for the pure vanillin and *o*-ethylvanillin in argon using a high pressure view cell, supplied by SITEC (Sieber Engineering AG, Zurich, Switzerland).

A static-analytic method was used for measuring solubilities of vanillin and *o*-ethylvanillin in argon. A detailed description of the experimental procedure is presented in literature [5].

The solubility of β -carotene and triolein were measured by using a high pressure, variable-volume cell (NWA GMBh, Lorrach, Germany). The cell is made of stainless steel (AISI 316) with adjustable internal volume between (30 and 60) cm³ by means of a piston. The piston is connected to a hydraulic pressurization system and allows operating conditions up to 750 bar and 200 °C. The pressure was measured by electronic pressure gauge (WIKA to $\pm 0.1\%$). The cell is provided with two sapphire windows for visual observation of the interior, a thermocouple for temperature monitoring (accurate ± 0.5 °C) and two valves for loading and discharging the gas. The cell contains a blade-turbine stirrer to mix the phases and two 60 mm electric heaters inserted in the stainless steel coat of the cell.[6]

High pressure extraction unit

Extraction experiments were performed on extraction unit presented in Figure 1. The plant is operating up to pressure 400 bar and temperature 100°C.

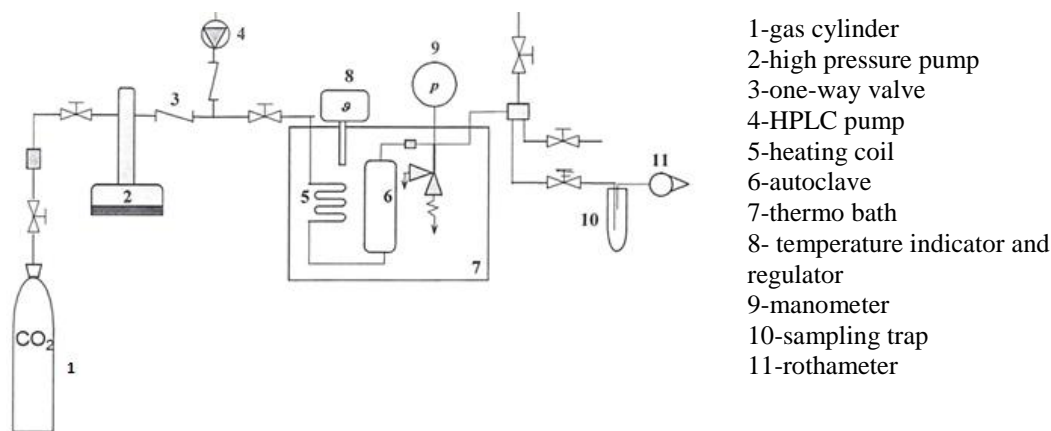


Figure 1: High pressure extraction apparatus

Methods

Phase equilibrium measurements

The view cell was first loaded with approximately 10 mL of homogeneous β -carotene and triolein mixture. Three different mass fractions of β -carotene ($w = 0.02$, $w = 0.05$, $w = 0.1$) were used for phase equilibrium measurements in CO_2 . Afterwards gas was introduced in the cell and system was heated up to 40 °C. The mixture was stirred, left to rest until it reach equilibrium and then samples were collected from both CO_2 rich phase and CO_2 pure phase. The samples were introduced in a flash separator set at atmospheric pressure. The amount of the sample was determined gravimetrically and the volume of realised gas was measured volumetrically by using graduated cylinder. The amount of β -carotene in the samples was measured by UV spectrophotometry.

Solubility of pure β -carotene was measured in propane and comparison with solubility of β -carotene in CO_2 was made.

Extraction experiments

SC extraction

Extractions of milled vanilla pods were performed with argon and CO_2 for a comparison at temperatures of 25 °C, 40 °C and 60 °C and pressures from 150 bar up to 300 bar. A detailed description of the method is given by Hadolin [7].

RESULTS

Solubility data

System in the cell could be observed during measurements through the sapphire window of the cell (Figure 2). Maximal solubility of vanillin has been obtained at a temperature of 40°C and a pressure of 438 bar, approx. 0.015 g/g of gas.



Figure 2: View to high pressure cell for the system of vanillin in argon at a pressure of 150 bar and at a temperature of 40°C.

Solubility is higher in case of lower temperatures and also a high impact of pressure is noted up to about 200 bar. With additional increase of pressure only a slight impact on solubility is observed. In comparison to solubility of the substance in CO₂ solubility is higher in argon at lower temperatures and pressures up to about 200 bar. Again, an increase of pressure does not exhibit a noticeable impact on solubility (Figure 3).

For *o*-ethylvanilin in argon highest solubility was measured at pressures above 300 bar and at lower temperatures; about 0.5 g/g of gas. In comparison, solubility of *o*-ethylvanilin in CO₂ is lower, approx. 0.18 g/g of gas at a temperature of 60°C and a pressure of 300 bar.

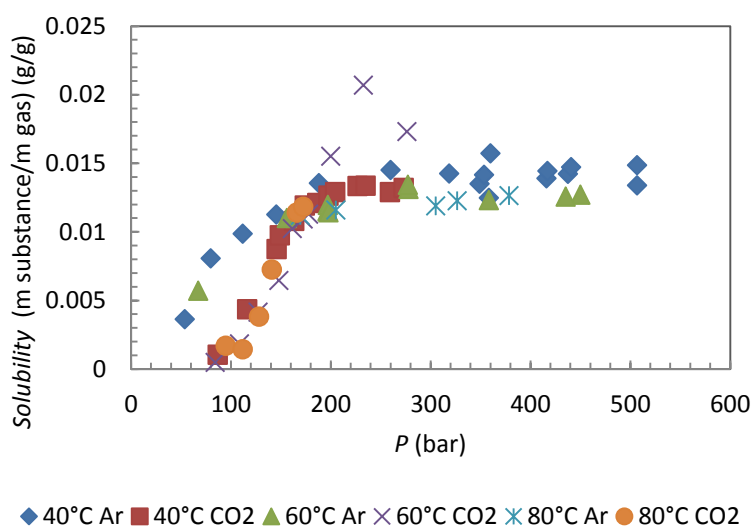


Figure 3. Solubility of vanillin in argon and in CO₂ [4].

A comparison of the solubility data of pure vanillin and *o*-ethylvanilin in argon and in CO₂ was done and it can be concluded that solubility is higher in argon at lower temperatures and pressures up to about 200 bar.

Ternary system β -carotene – triolein – CO_2

The experimental solubility data for β -carotene and triolein from the ternary β -carotene - triolein - CO_2 system are presented in Figure 3 separately for each component as a pressure in MPa versus solubility in $\text{mol}\cdot\text{mol}^{-1}$.

From Figure 3b it can be seen that the solubility of triolein in the upper rich phase increases with increasing pressure up to 50 MPa at constant temperature of 40 °C and decreasing with increasing pressure at the constant temperature in the lower phase in all pressure range. All isotherms for each phase has similar trend of solubility. Above the 500 bar can be observed drop in solubility of triolein (Figure 4b). Different mass fractions of β -carotene in the mixture lead to higher solubility of triolein in the upper phase. Solubility increases with increasing mass fraction of β -carotene in the upper phase Figure 4b and decreases with increasing mass fraction of β -carotene in the lower Figure 4a.

Increasing of the solubility of β -carotene in the upper phase (Figure 4d) and decreasing in the lower phase (Figure 4c) can be observed in all pressure range from 200 bar to 650 bar. Also the higher mass fraction of β -carotene in the mixture (Figure 4d) leads to higher solubility of β -carotene in the upper phase.

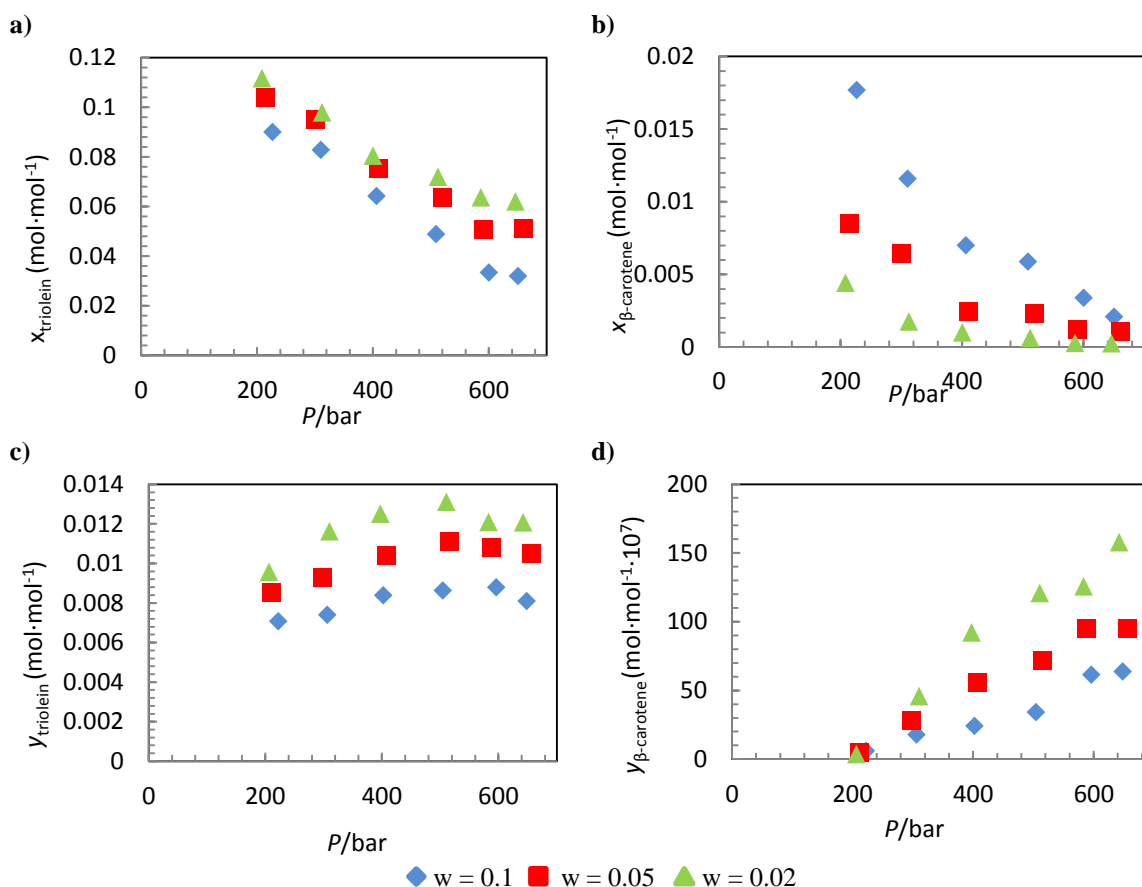


Figure 4: Solubility (x – lower phase, y – upper phase in $\text{mol}\cdot\text{mol}^{-1}$) of β – carotene and triolein in supercritical CO_2 at different mass fraction of β -carotene in triolein and in the pressure range from 200 bar to 650 bar at temperature of 40 °C.

Binary system β -carotene – CO_2 and β -carotene – propane

Also two binary systems were investigated at temperature of 40 °C. In both examples on the Figure 5 can be seen that solubility of β -carotene increases with increasing pressure. The solubility was five times higher when propane was used as a solvent. Also propane requires lower pressure for getting higher solubility results in comparison with CO_2 . Reason for that is in polarity of the solvent. β -carotene is completely non-polar molecule and it has high molar mass and specifically shape because of that is just slightly soluble CO_2 which is also non polar. But propane even is more non-polar as CO_2 due to this the solubility of β -carotene is higher.

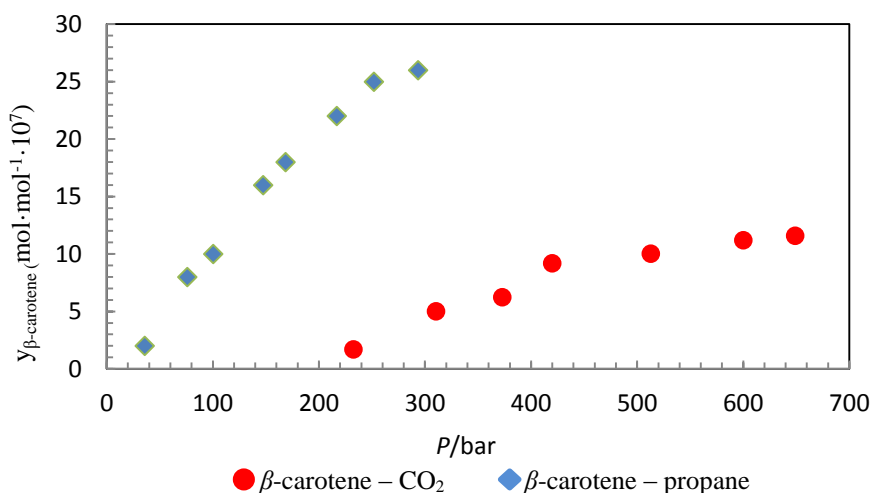


Figure 5: Solubility y (mol·mol⁻¹) of β -carotene in CO_2 and propane at temperature 40 °C.

Extraction experiments

SCF extraction

Kinetic curves obtained at a constant pressure of 300 bar demonstrate impact of temperature on the extraction yield. The highest yield in case of SCF extraction with CO_2 was observed at 25°C and 300 bar (5.7%) as demonstrated in Figure 6 a.

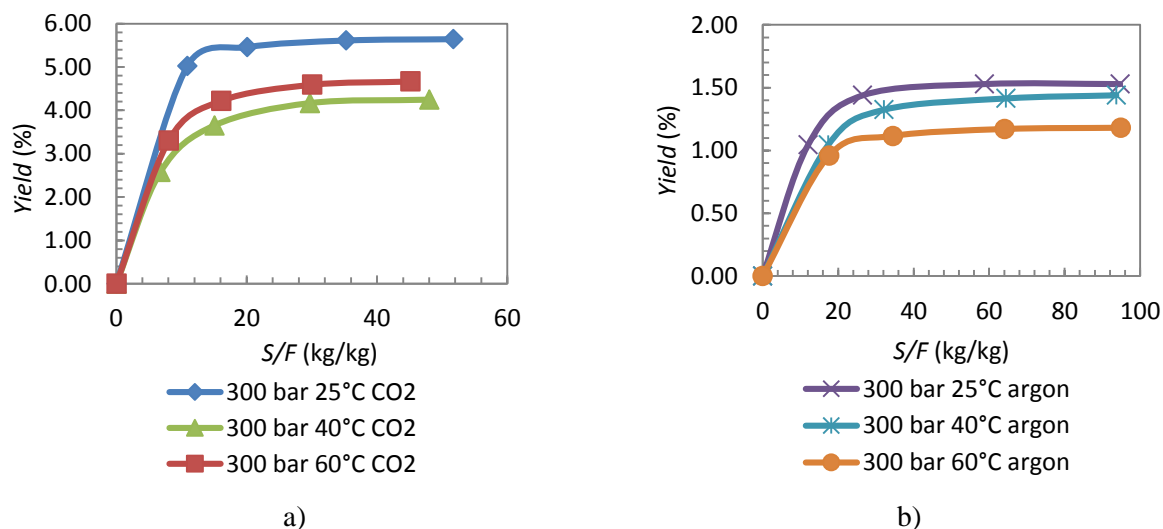


Figure 6: a) Kinetics of semi-continuous extraction of vanilla pods with CO_2 at temperatures of 25 °C; 40 °C and 60 °C at a pressure of 300 bar, b) Kinetics of semi-continuous extraction of vanilla pods with argon at temperatures of 25 °C; 40 °C and 60 °C at a pressure of 300 bar.

For both gases higher extraction yields are obtained in case of higher pressure, but when comparing extraction yields obtained with both solvents, yields are higher in case of CO₂. On the other hand, yield decreases with an increase of temperature in case extraction with argon. The highest yield in case of argon is observed at 25 °C and 300 bar (approx. 1.53 %) as presented in Figure 6 b, where kinetics curves of semi-continuous extraction of vanilla pods with argon at temperatures of 25 °C; 40 °C and 60 °C at a pressure of 300 bar are provided.

UV spectrophotometric analysis of extracts indicate high content of vanillin in extracts, obtained by extraction with supercritical fluids either with CO₂ or argon (up to 88 wt. % of vanillin).

According to relatively high solubilities of vanillin and *o*-ethylvanilin in argon it can be summarized that argon is a suitable processing media also for artificial vanilins.

As vanilla extracts contain several compounds, approximately 200 substances main compounds are 4-hydroxy-benzaldehyde, vanillic acid and 4-hydroxybenzoic acid in addition to vanillin, a raw preliminary evaluation of obtained extracts is presented in present work.

CONCLUSION

Processing of natural products with supercritical fluid technologies has been an extensive area of research during the past two decades. CO₂ and water have been the most used supercritical fluids. Even if water is the cheapest solvent, due to the high polarity, the use of water as recrystallization solvent is limited and therefore the second cheapest solvent with pressure and temperature tunable properties is carbon dioxide, followed by several gases with a high potential to be applied as supercritical fluids. Nowadays, the trends shift towards the use of unconventional supercritical fluids, such as SF₆ and argon. Propane, as a very selective solvent for supercritical extraction, has recently been intensively applied. 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. However, there is no doubt that the use of supercritical fluids has a bright future, particularly for the products for use in cosmetics, pharmaceuticals and food industry where high quality and high value products are required. There are also several new topics which are developing to the commercial scale. Many applications such as high pressure sterilization, jet-cutting, thin film deposition for microelectronics, and the separation of value-added products from fermentation broths in the biotechnology field have been fully developed and commercialized.

Additionally, there are many advantages of supercritical fluid processing under “real” high pressure like new product formulations and economic production of high value products due to the fact that the solubility of several dense gas low soluble substances increases with increasing pressure and temperature. Since higher pressures enable economically feasible extraction of substances from natural tissue, the future reasearch will most probably lead towards investigation of the fundamental thermodynamic data required to design such processes.

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