

SEPARATION OF SUBSTANCES FROM HIGHLY VISCOUS SYSTEMS BY HIGH PRESSURE EXTRACTION PROCESSES

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Abstract:

Separation or formulation of products by supercritical fluids and production of substances and composites with unique properties and characteristics for the use in different applications are nowadays intensively studied. One of the most important advantages using supercritical fluids is selective extraction of components or fractionation of total extracts.

As yet, industrial dense gas extraction process units were used with maximum operating pressure up to 750 bar, but usual operating pressure was up to 500 bar. From literature it is known that the total yield increases with increasing pressure, due to higher solubility of substances in dense gases and, furthermore, for less soluble substances co-solvents (entrainers) could be used. Of late, in addition to previous installations, also a small scale plant designed for ultra high pressure (2.500 bar) extraction and selective multi-stage fractionation of substances from plant materials is in operation.

Highly viscous systems were mostly processed using conventional solvents for viscosity reduction. The main disadvantage using conventional solvents is that the extracts are contaminated with organic solvents which can not be easily removed. The legal limitations of solvent residues and solvents (for products for use in human applications) and isolation/fractionation of special components from total extracts in combination with different formulation and sterilization processes will increase the use of dense gases for extraction applications.

Examples on selective extraction of components from highly viscous systems like separation of lecithin from degumming residues and others will be presented. Also fundamental data on phase equilibrium for these systems as well as process and mechanical design of equipment and economy of the process will be dealt with.

Key words:

high pressure, dense gases, supercritical CO₂, extraction, highly viscous substances

INTRODUCTION

Design of new products with special characteristics or designs of new processes, which are environmentally friendly and have an impact to sustainable processes, are a great challenge for chemical engineers.

In the man's living environment the pressure ranges between 0.25 bar at the highest mountain up to 1000 bar at the bottom of deepest ocean. Since mankind mostly lives at the globe surface the first technologies for production of various substances were operated at atmospheric pressure. In the early 20th century the demand for new products like ammonia or methanol shifted the technological processes towards higher pressure.

High pressure as a relatively new tool gave in several processes completely new products with special characteristics. Several new processes are environmentally friendly, of low costs and sustainable.

Checking literature and patent filings reveals that the majority of patents and patent filings on extraction are dealing with separation of actives from plant material as such. [1], [2].

There are fewer activities presented on isolation/fractionation of components from liquids or highly viscous systems.

Extraction of highly viscous systems with supercritical fluids is comparable to liquid-liquid extraction, where compressed gas is used instead of an organic solvent. In extraction processes of highly viscous systems the pressure plays an important role. Changing pressure and/or temperature, the physico-chemical properties of the SCF, like density, viscosity, surface tension, dielectric constant, etc. are changed. Selective extraction of components or fractionation of total extracts is possible by use of different gases for isolation/fractionation of components and/or changing process parameters. Another advantage is that depending on the feed material the density difference between the two counter-currently flowing phases can be adjusted. Adding of dense gas to highly viscous systems could reduce the viscosity of such systems.

One of the most important advantages of using supercritical fluids is the simple solvent regeneration in comparison with liquid-liquid extraction, where in most cases solvent regeneration includes a re-extraction or distillation step, which is energy consuming and therefore cost intensive. Heat treatment of extract or raffinate phase may causes degradation of heat sensitive substances. For extraction plants using SCFs the solvent regeneration is achieved by changing pressure and/or temperature after the extraction step, thus changing the density and by it the solvent power of the gas, which can be later easily recycled after separation of solute.

Compared to extraction of solids with SCF, highly viscous systems could be continuously fed in and withdrawn from the high pressure extraction unit. This gives the benefit of higher throughputs in continuous operating counter current processes.

Literature search shows some laboratory scale studies on extractions in the systems liquid/supercritical fluid. Several data on binary systems liquid/SCF could be found, but there are less data on systems liquid/liquid/supercritical fluid which are necessary for design of extraction processes of liquid mixtures with supercritical fluids.

OPERATION METHODS AND APPARATUS

Like in conventional continuous liquid-liquid extraction in extraction of highly viscous liquid systems/sub- or supercritical solvents extraction several modes of operation are available. Single-stage separation is the simplest one and is used for the systems where separation factors for the solute are high. Multi-stage separation is necessary when the separation factor between components is in the order of 1-10. Different modes of operation of multistage processes are used like counter-current extraction, multistage co-current extraction and multistage cross-flow extraction where relatively low loading of solvent with extract are obtained in each stage.

In multi stage counter-current extraction high loading of solvent with extracts is possible as well as different geometry of apparatus is possible.

In a spray extraction process the flow sheet of apparatus is similar to that for conventional solvent systems. In this type of process the feed is usually liquid or highly viscous liquid which contains solute and other non dense gas soluble component. The system is sprayed into an extractor operated under certain pressure and temperature. At these conditions a certain amount of solute substance is solubilized in the gas and is separated as solute in separator. The remaining raffinate is concentrated on gas insoluble substances and as such is concentrated in the extractor.

Counter-current liquid/sub- or supercritical fluid extraction or counter-current highly viscous liquid/sub- or supercritical fluid extraction can be modeled by the use of typical commonly used basic equations: mass balance, energy balance, equilibrium distribution coefficients and mass transfer rate equations. For extraction, following data is necessary:

- determination of number of theoretical stages/transfer units,
- size and type of a separation device with respect to separation performance,
- design of solvent cycle.

Based on the above facts and experimental data the costs of separation using liquid/sub- or supercritical process can be determined.

EXAMPLES

Soy Lecithin

Lecithin is a natural emulsifier, which is found in high concentrations in egg yolk and soy beans [3]. It is used as a nutraceutical, as emulsifying agent in the food industry and as a source for phosphatidylcholine (PC) in the pharmaceutical industry. Mainly used in the food industry is soy lecithin, while egg yolk lecithin is used to recover PC, because the PC-content in egg lecithin is higher than in soy lecithin. Lecithin is not a single substance rather than a mixture of different phospholipids: phosphatidylcholine (PC), phosphatidylethanolamin (PE), phosphatidylinositol (PI), phosphatoic acid (PA) and others [3], [4]. Soy lecithin is a by-product of the soy bean oil production. Raw soy bean oil is usually extracted by hexane. In the first refining step gummy substances are removed by hot water and collected as de-gumming residue. Further refining steps such as hydrolysis, bleaching and others lead to the fine oil. De-gumming residue is dried giving raw lecithin as the product.

Different lecithin products are produced. The first is the liquid lecithin, which is a highly viscous fluid with a typical content of 62 % of acetone insoluble matter (AIM), the parameter for the purity of lecithin. This liquid lecithin is conventionally de-oiled by acetone to form a pure lecithin in powder or granular shape with AIM-content of approx. 97 %.

To overcome the problems with the use of acetone, residues in the de-oiled lecithin and the extracted oil needs thorough solvent recovery, plants have to be explosion-proof. Supercritical CO₂ processing of de-gumming residue could be an alternative. The demand of green products requires the use of a green solvent - like CO₂ [5]-[8]. Up to now all these process developments led to processes which were not applied in industrial scale, besides the process using propane [9], [10].

A development was started to establish a feasible process leading to a production scale plant using CO₂ which produces lecithin powder with a minimum content of 95 % AIM.

LABORATORY SCALE EXPERIMENTS

The studies started with solubility measurements in a phase equilibrium apparatus on a real de-gumming residue (DR) containing 50 % AIM. Determined was the solubility of the soy bean oil in CO₂ as well as the solubility of CO₂ in the soy bean oil.

PHASE EQUILIBRIUM DETERMINATIONS

Variable volume high pressure view cell was supplied by NWA (Lörrach – D). Maximal volume of cell is 60 mL and is designed for maximum operating pressure of 700 bar, and maximum operating temperature of 250 °C. The main advantage of this design is that the pressure during sampling procedure is kept constant. By moving the rear glass (sapphire) by means of a hydraulic system connected to the apparatus, the volume of the cell was reduced during sampling procedure. Movement of rear glass is very precise, and thus very fine pressure adjustments (1 bar accuracy) can be maintained. View cell is also equipped with a propeller stirrer, where stirring can be regulated. Flow sheet and photo of the cell is presented in Figure 1.

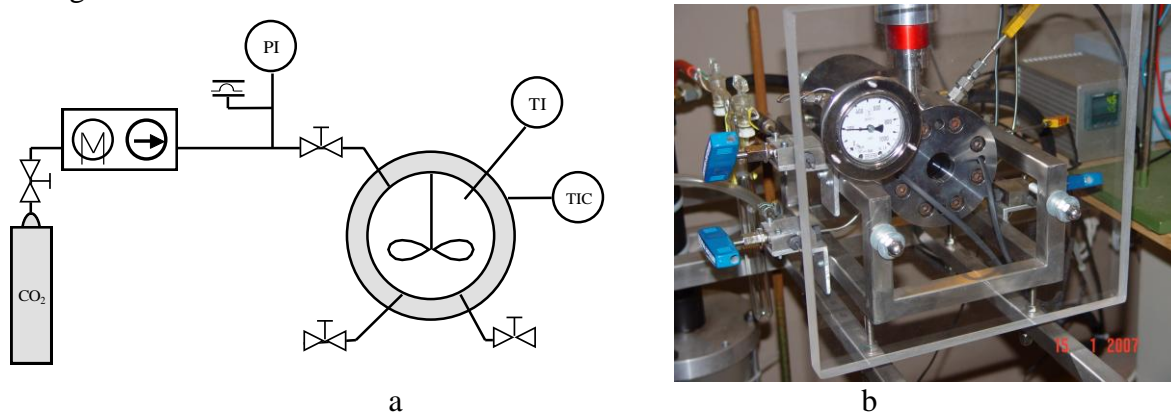


Figure 1: High pressure view cell: flow sheet (a) and photo (b) of the apparatus

Solubility of oil in CO₂ and on solubility of CO₂ in oil

Preliminary solubility measurements were performed in pressure range up to 600 bar and at temperatures 40 and 60 °C. The apparatus used was high pressure view cell (60 mL, 700 bar, 250 °C). 25-30 g of DR was introduced into the view cell and pressurized with CO₂ to desired pressure. Stirring and settling was applied for 1 h each, and samples of lower and upper phase were taken.

As shown in Figure 2 and Figure 3 the solubility of oil in CO₂ as well as the solubility of CO₂ in oil increases with increasing pressure and temperature. A solubility maximum in the applied pressure range was not observed for the solubility of oil in CO₂.

Results are given as mg of oil per g of CO₂ for the upper (gaseous) phase and mg of CO₂ per g of DR for the lower (liquid) phase. On the mass basis, results are also given as weight % of CO₂ in liquid (left side of diagram) and in gaseous phase (right side of diagram) and are shown in Figure 3. The solubility of CO₂ in DR increased up to approx 30 wt. % at 325 bar and remained constant up to 600 bar. The maximum wt.% of oil in CO₂ was obtained at 1.5 wt.% of oil.

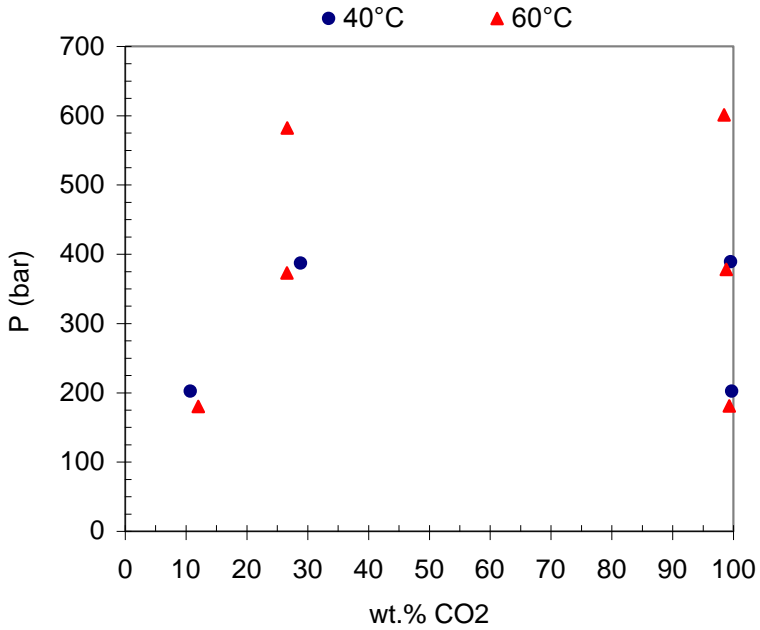


Figure 2: P-x diagram for the system degumming residue/CO₂ (CO₂ in oil and oil in CO₂)

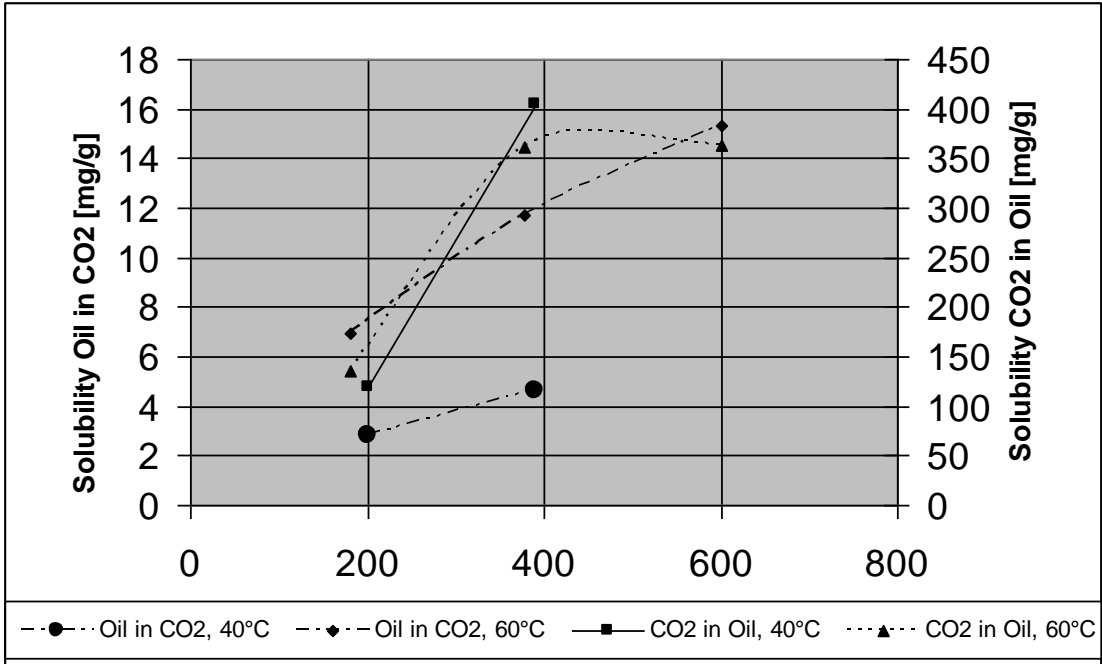


Figure 3: Solubility data for the system degumming residue/CO₂

Phase behavior observations of system DR-CO₂ in view cell

High pressure view cell was filled with de-gumming residue and was pressurized with CO₂ to a certain pressure. Temperature was set to desired value and the system was pressurized to desired value. Mixture was stirred and left for the phases to separate, during which phase behavior was observed.

Influence of process parameters on:

- Distribution of liquid and gaseous phases – possible phase inversions,
- Qualitative evaluation of viscosity of mixtures,
- Separation of phases after intensive stirring was observed.

In the range of applied pressure and temperature (up to 520 bar at 62 °C and 700 bar at 40 °C) the distribution of phases was such that DR rich phase (liquid phase) was the bottom phase and CO₂ rich phase containing dissolved oil (gaseous phase) was the upper phase. No inversion of phases was observed as could be seen from Figure 4.

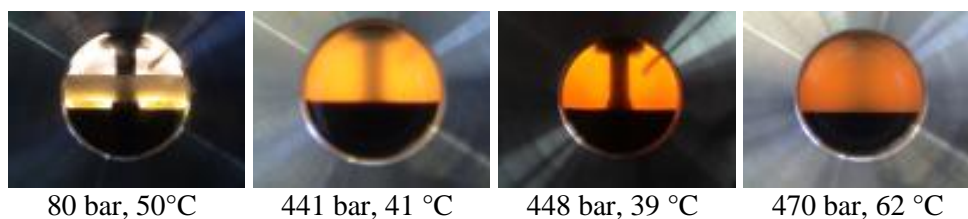


Figure 4: Phase observations in system degumming residue/CO₂

It was found that the viscosity of system was reduced with increasing pressure at constant temperature and at constant pressure the viscosity was reduced with increasing temperature. The separation of phases was fast after intensive mixing.

LAB SCALE EXTRACTION EXPERIMENTS

From the results of the solubility measurement the conditions for the experiments in the next scale were fixed. The experiments were carried out in a 10 L laboratory plant with a maximum operating pressure of 750 bar. Extraction was carried out in the way that the de-gumming residue is fed at the top into the extractor and is counter-currently extracted by CO₂, which is fed at the bottom of the vessel. The extracted oil is recovered in the separator while the de-oiled powder is collected in the extractor. The flow diagram of the experimental extraction set up is presented in Figure 5.

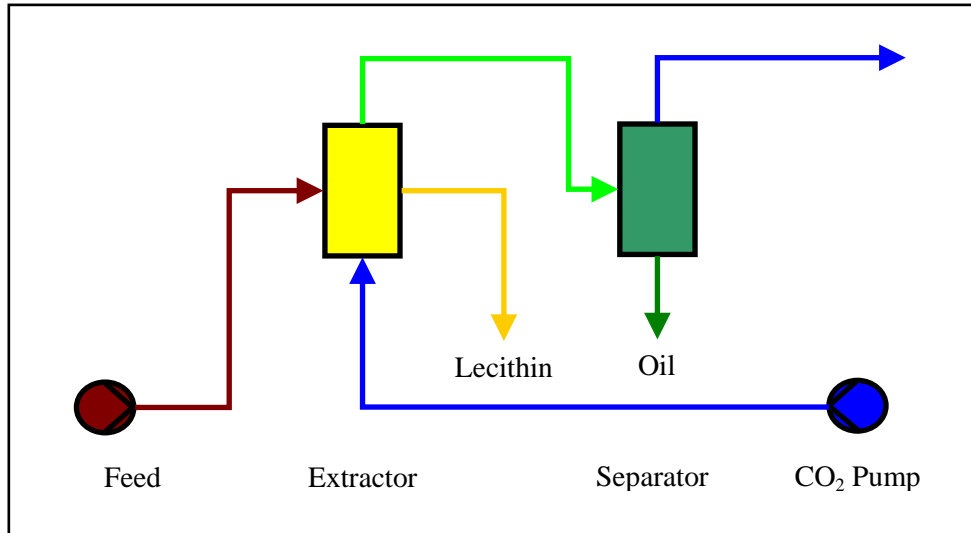


Figure 5: Principle flow diagram.

Tests were carried out at 400 bar and 500 bar at a constant temperature of 60 °C. The specific CO₂-flow rate, which is defined as kg of CO₂ per kg of raw material, was varied between 75 and 225 kg/kg. As raw material the same de-gumming residue as for the solubility measurements is used. The results of all experiments are shown in Figure 6. As the target the content of AIM was analyzed. As can be seen from Figure 6 the AIM-content in the de-oiled product is widely independent from the specific CO₂-demand at the tested condition. Also the tests led to a powder product as shown in Figure 7.

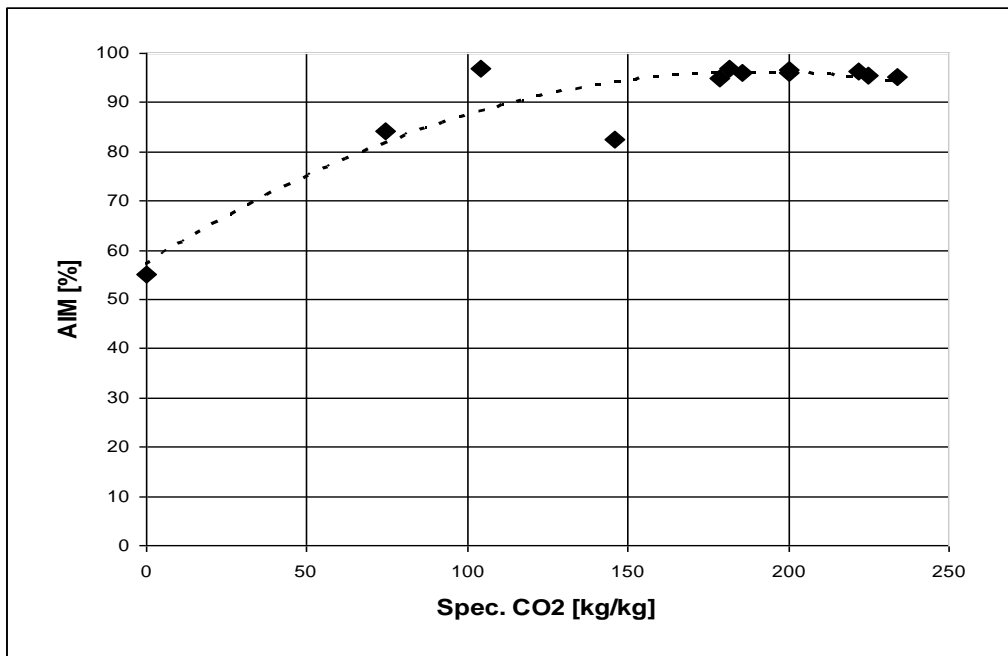


Figure 6: Results of Lab-scale tests

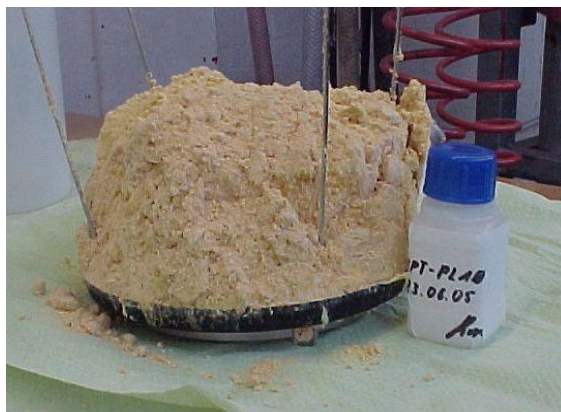


Figure 7: Lecithin powder from Lab-scale tests



Figure 8: Small scale production plant for Scale-up tests

PILOT – SMALL SCALE PRODUCTION TESTS

The results from the tests in the laboratory plant, pressure, temperature, CO₂-flow rate were used for scale-up tests in a small scale production plant, which is shown in Figure 8. This plant can be operated up to an extraction pressure of 500 bar at a CO₂-flow rate of 1,000 kg/h. The tests were carried out as described above at 400 bar and 60 °C with specific CO₂-flow rates ranging from 100 kg/kg to 200 kg/kg.

During all test runs totally 200 kg of de-gumming residue were extracted resulting in approx. 100 kg of lecithin powder. As it was found out during the lab-scale tests also the scale up tests show, that the extraction result is independent from the specific CO₂-flow rate in the range between 100 kg/kg and 200 kg/kg.

Besides the degree of de-oiling also the target of producing a powder was reached. Figure 9 shows the product which is collected after the de-oiling process.

During the experimental study a safe design basis for production plants was established. The experiments range from a scale of some ml to 200 L extractor volume. In every scale it was demonstrated that both of the targets, high degree of de-oiling and a powder product, can be reached.

PRODUCTION PLANT DESIGN, CONSTRUCTION AND START UP

As the result of the experimental studies a production plant was designed based on the parameters, which were obtained and verified in different scales. This plant has to de-oil 200 kg of liquid lecithin per hour. Assuming 62 % AIM in the raw material approx. 120 kg/h of

pure lecithin powder will be produced. Beside the degree of de-oiling and the powdery shape it is essential to prevent oxidation in the final product.



Figure 9: Product from production scale tests

For the production plant a continuous feeding of the raw material and extraction is applied. Because the product is a solid material, de-oiled lecithin powder, the extractor has to be emptied batch-wise during the extraction without interruption of feeding. This has the advantage of being a more effective and economic operation of the de-oiling process and ensures that the sensible product will not come into contact with oxygen from air. The plant will be operated at extraction pressures up to 500 bar and should produce a “green” bio- lecithin or lecithin powder from non-GMO soy beans.



Figure 10: Product take-off from production plant

Concentration of Phospholipids (PL) from natural concentrate

On similar laboratory scale apparatus as presented in previous chapter, phospholipids concentrate which contained approx. 18.7 wt% of phosphatidylcholine (PC), 2.4 wt% of phosphatidylinositol (PI), and 6.1 wt% of phosphatidylethanolamin (PE) was further concentrated in a process where raw product was spray extracted with supercritical CO₂.

Extraction experiments were performed at pressures between 350 bar and 450 bar while the extraction temperature was varied between 30 °C and 100 °C. The ways of contacting of flow of PL concentrate and flow of CO₂ were also different. The influence of different process parameters on the purity and yield was studied. Phospholipids were concentrated in raffinate, while the oils waxes and other compounds were collected in extract.

In series of experiments, process parameters were optimized and a raffinate containing approx. 46.5 wt% of phosphatidylcholine (PC), 4.4 wt% of phosphatidylinositol (PI) and 2.1 wt% of phosphatidylethanolamin (PE) was obtained.

It can be concluded that for concentration of phospholipid components in raffinates of PL concentrate with spray extraction with CO₂ should be performed at pressure between 350 bar and 450 bar while the extraction temperature should be 30 – 100 °C

Generally we could conclude that the total yields increases with increasing pressure of CO₂ at all temperatures. Based on experiments it is evident that at temperature 40°C the extraction yields are low probably due to the fact that the system is too viscous. After pressure reduction the vessels are full of foaming very highly viscous liquid which could not be removed from the vessels. We could also conclude that the total yields increase with increasing S/F holding constant all other process parameters.

Lycopene

On similar apparatus as presented in previous chapter tomato CO₂ extract with total carotenoids content 0.88 wt% and tomato CO₂ extract with total carotenoids content 1.03 wt% were further concentrated in a process where extract was again extracted with supercritical CO₂.

Carotenoids were concentrated in raffinate, while the oils, waxes and other compounds were collected in extract.

The process parameters and extraction yields as well as concentrations in extracts and raffinates were varied. In series of experiments process parameters were optimized and a concentrate with total carotenoids content of 17.88 wt% of total carotenoids was obtained.

We could conclude that for concentration of carotenoids in raffinates of tomato extracts with re-extraction with CO₂ at extraction pressure 100 bar to 200 bar and temperature 40 °C S/F should be relatively high – over 200. Of course, with higher S/F also carotenoids were co-extracted. Higher extraction pressure should need lower S/F, but also more carotenoids were co-extracted.

It could be concluded that from tomato residue CO₂ extracts carotenoids could be efficiently concentrated in raffinate by re-extraction at pressure 100 bar and 200 bar and temperature 40°C. The influence of extraction temperature was not investigated and therefore it seems necessary to further optimize the process parameters for re-extraction of tomato residues CO₂ extracts.

CONCLUSIONS

It is evident that the applied processes were suitable for separation/fractionation of components from highly viscous systems.

For concentration of lecithin from degumming residue the industrial plant was installed, the plant was started up and production tests were carried out. The parameters applied for the de-oiling were the minimum figures found out in the experimental studies. In all tests the minimum requirement on de-oiling was fulfilled. The content of acetone insoluble matter reached 95 % and even more.

For concentration of phospholipids from natural concentrate by spray extraction experiments different geometries of apparatus were tested. Very high efficiency of different processes was determined. Highly concentrated products with high phospholipids content were obtained.

Carotenoids were successfully isolated from ultra high pressure extract. Highly concentrated product with high total carotenoids content was obtained.

The costs per ton of the feed of liquids are influenced by throughput and mode of operation (batch process have higher operating costs while in continuous the process costs are lower) and are in the range from ca. 60 €/kg feed of liquid at throughput of ca. 200 t per year in batch process down to approx. 0.06 €/kg feed at throughput ca. 60.000 t per year for continuous process.

In the literature [11] it is reported that common estimation methods for the costs of separation of liquid systems with CO₂ per ton of the feed of liquids yield results with an error of ±30%, while even after the project has been completed, costs are difficult to be determined better than 5% error.

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