Supercritical carbon dioxide extraction of plant materials at ultra high pressure

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In recent years numerous developments were asked for by demanding industries (e.g. automotive, chemical, petrochemical, food, pharmaceutical, etc.). These developments comprise remarkable increase in single train capacities of production plants and/or rise in operating pressure.

Examples from commercial applications of high pressure technologies in production of fertilizer and LDPE, in food processing as well as with the transfer of know-how of high pressure processing into new fields like pharmaceuticals and semiconductor industry are known.

For extraction applications a trend to higher pressures is visible which can be demonstrated by the design pressure of recently delivered plants. The paper will describe said developments briefly and lead to explanations of the advantages of supercritical fluid processing at “real” high pressure like new product developments and economic production of high value products.

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

INTRODUCTION

Industrial production is continuously driven by ongoing improvements looking for the most economical solution of producing the goods. This driving force is founded on steady development of new processes or production techniques, economies of scale as well as optimization of the energy demand during production. Some examples can be given from the automotive industry, chemical and petrochemical production as well as from mechanical engineering and food processing.

Comparing these trends and developments in various industries with R&D efforts as well as industrial applications of SFE we see some differences. The early industrial application of SFE (decaffeination of coffee, hops extraction) was a big step forward using approx. 300 bar processes in relatively large scale up to 20 m³. Thereafter we do not find too many new processes using higher pressures or larger scale. R&D often focus on process development at so-called high pressure meaning 80 – 150 bar instead of really challenging technical possibilities.

Figure 1 shows the development of plant capacities by region. Although we see additions of plants in Asia (mainly China), one of the largest plants built reaches only up to a vessel volume of 3x 3.500 l at maximum operating pressure of 500 bar. This is nothing unusual or exciting.

Is processing with supercritical fluids under high pressure too expensive? When doing calculations of processing cost and comparing the findings of different models and authors, we find the decrease of cost with higher operating pressure as in other processes and industries, but – interesting enough – we do not operate all plants at their economic optimum. Moreover, we hardly find plants that can be used to give evidence.

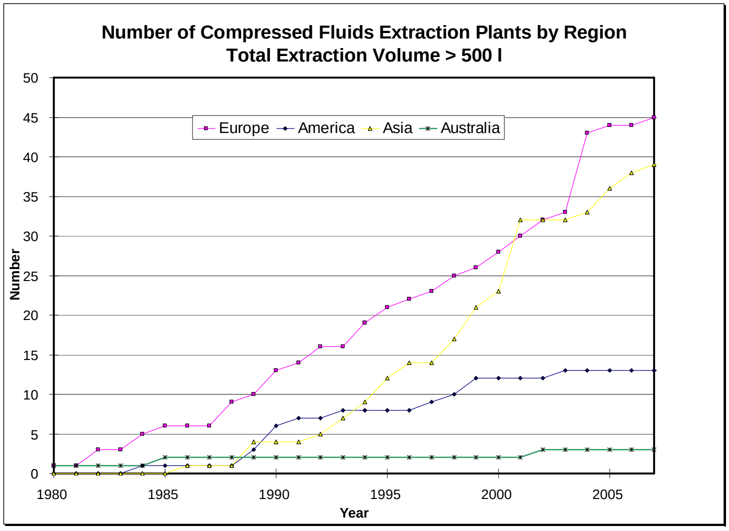
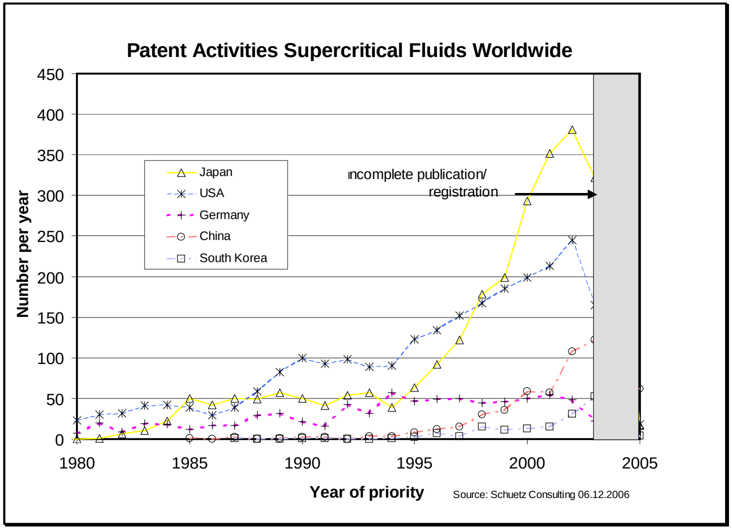

Number of Compressed Fluids Extraction Plants by Region
Total Extraction Volume > 500 l

Figure 1: Development of SFE plant capacities by region

So far only one production plant (3 x 150 l) in the US is operating at pressures up to 700 bar and 1 extractor (100 l volume) is known at Nateco2 in Germany having done a special development at pressures up to 1.000 bar. A first installation for China using 750 bar in a plant consisting of 3 autoclaves of 200 l net volume is currently completed.
Checking literature and patent filings we can derive the diagram shown in Figure 2. There is no trend clearly directing towards higher pressures. However, with a little sigh of relief, we can at least imagine a split in process pressures. Part of the work is trying to reduce the pressure, while another part of work is looking into the benefit of “real” high pressures.


Patent Activities Supercritical Fluids Worldwide

Source: Schuetz Consulting 06.12.2006

Figure 2: Pressures used for R&D and patent filings of SFE processes

UHDE HPT executed “real” high pressure extraction tests with CO_2 as solvent for many different raw materials on a multipurpose extraction plant being suitable for extraction up to 2.500 bar [1].

PHASE EQUILIBRIUM DATA AND MASS TRANSFER DATA

From the literature [2, 3] it is well know that the solubility of substances increases with increasing pressure and temperature. Therefore the total yield increases, but the selectivity for a certain substance decreases. It is also known that at constant temperature and increasing pressure solubility maximum is reached and afterwards with increasing pressure the solubility decreases. Such substances are for example soy oil and jojoba triglycerides, where the solubility decreases at certain temperature already after pressure of 600 bar [4].

Several patents could be found where higher pressure is used for separation of substances from plant material. In patent [5] a pressure for separation of caffeine from tea is described. Applied pressures were up to 1000 bar and temperature up to 80°C. Isolation of Xanthohumol rich hop extracts at 60 °C is described in patents [6, 7]. For industrial application pressures over 500 bar are unusual and most of the industrial plants operate at pressures of 300 to 500 bar [8-10].

Due to the relatively low solubility of substances in this pressure range (up to 500 bar) entrainers are added to CO_2, to enhance the solubility of substances. The disadvantage using entrainers is the contamination of extracts with organic solvents. Therefore, expensive separation processes have to be applied for separation of residual solvents, which could not be separated under certain limits.

ULTRA HIGH PRESSURE EXTRACTION EQUIPMENT

Figure 3: Ultra high pressure extraction unit

Gas extraction from solids as at low pressure extraction processes consists of two process steps: 1. the extraction, and 2. the separation of the extract from the solvent. In the extraction, the supercritical solvent flows through a fixed bed of solid particles and dissolves the extractable components of the solid. The solvent is fed to the extractor and evenly distributed to the inlet of the fixed bed. The loaded solvent is removed from the extractor and fed to the precipitator (separator). In this apparatus the direction of flow of the supercritical solvent through the fixed bed can be upwards or downwards.

Table 1: Technical characteristics of UHP extraction unit

	Parameter
Extractor 1	Volume: 0,64L Maximal operating pressure: 2500 bar Maximal operating temperature: 120°C
Extractor 2	Volume: 2.0L Maximal operating pressure: 2500 bar Maximal operating temperature: 120°C
Separator 1	Volume: 1.0L Maximal operating pressure: 1000 bar Maximal operating temperature: 120°C
Separator 2	Volume: 0.64L Maximal operating pressure: 1000 bar Maximal operating temperature: 120°C
Flow rate of CO_2	Max 16 kg CO_2/h

EXAMPLES

Rosemary

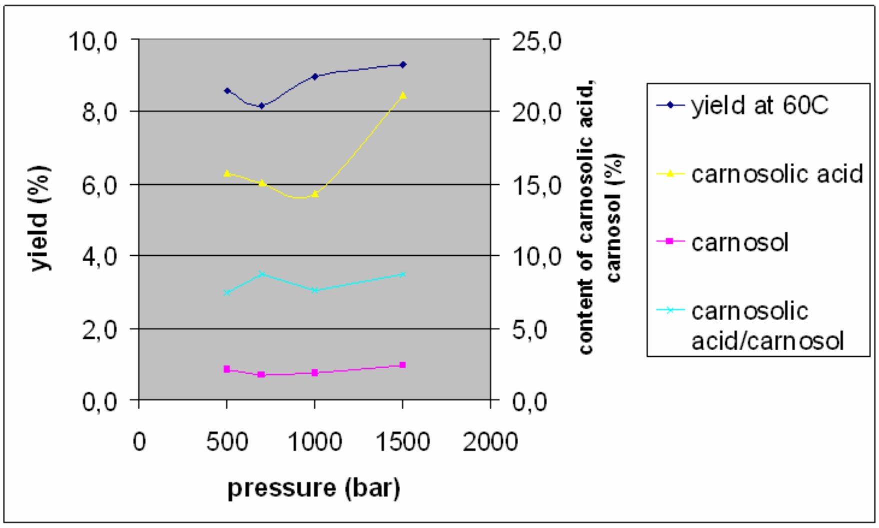


Figure 4: Total yield of rosemary extraction and composition vs. pressure at 60°C and S/F=40kg/kg

On figure 4 the effect of extraction pressure to the yield and composition for rosemary extraction with CO2. The carnosolic acid content of the extract can be varied to a high degree when changing the pressure between 1.000 and 1.500 bar. This phenomenon can be used to adjust the product composition in situ during the extraction processing step.

Generally we could conclude that extraction of rosemary with CO2 at temperature 80ºC gave highest yields and total yield on carnosolic acid and carnosol at highest applied pressure (1500 bar) and high S/F, but the total yield (at S/F=40) of carnosolic acid are lower than at temperature 60ºC and higher than at temperature 100ºC. With increasing S/F the total yield on carnosolic acid was the highest at S/F=60 and pressure 1500bar at temperature 80ºC.

At temperature 100ºC as could be seen from data in figures extraction yields increases with increasing pressure at constant ratio S/F ($m_{CO2}/m_{material}$) 40kg/kg from 500 bar up to 1000 bar, but the content of carnosolic acid decreases. With further increase of pressure from 1000 bar up to 1500bar the total yield decreases but the content of carnosolic acid in extracts increases.

The ratio between carnosolic acid/carnosol does not change with pressure, what confirms that no oxidation products of carnosolic acid during ultra high pressure extraction process are formed.

Nut kernels (Juglans regia)

Sliced nut kernels (Juglans regia) with oil content of about 58% (w/w) was filled into the extractor and extracted at temperature 40C and pressures 300 bar, 500 bar, 1000 bar and 1500bar. From results on Figure 5 it is evident that for the same yield the solvent/feed ratio is decreased with increasing pressure.

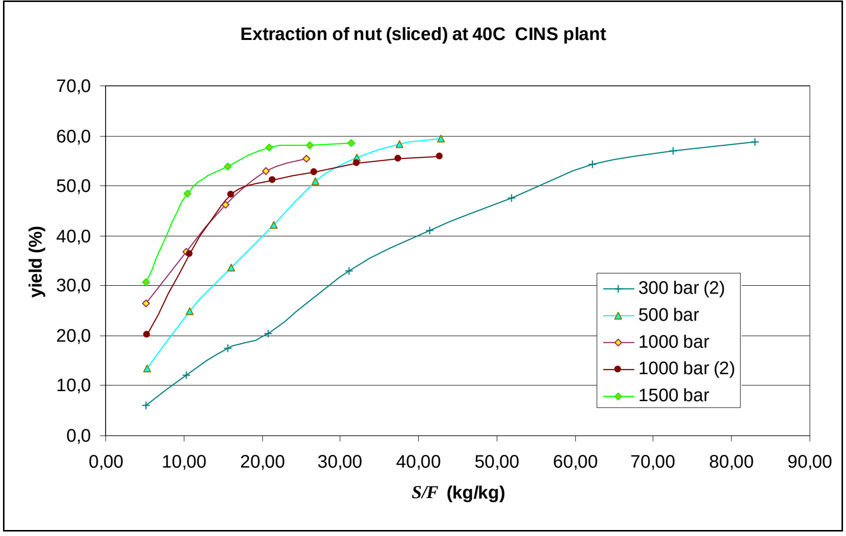


Figure 5: Yield vs. solvent/feed ratio for extraction of nut oil

CONCLUSIONS

Many active ingredients of plant material and other natural resources cannot be extracted using SFE at pressure below 500 bar. Either co-solvent are needed with the additional task to remove the co-solvent from the product. Therefore, more process development is needed and a first pilot plant capable of using pressures up to 2.500 bar is installed and operational. Economy of the process was studied in details and is shown in figure 6.

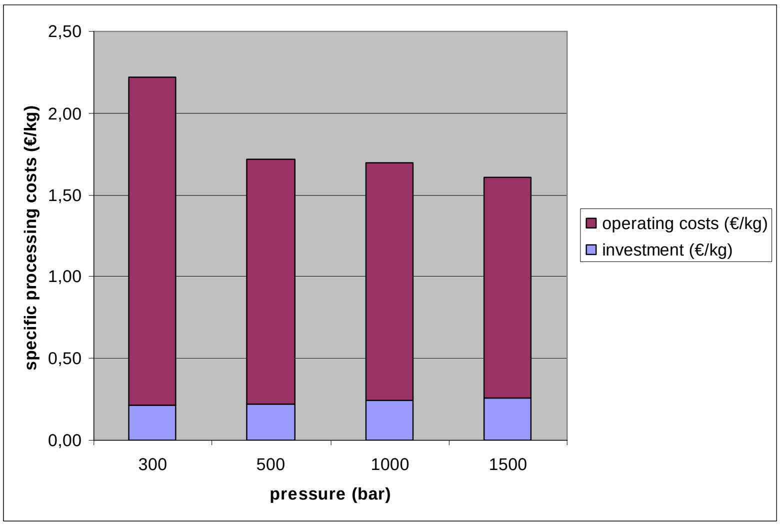


Figure 6: Economy of process vs. pressure

In our new invented process [11] a phenomena of decreased dense gas solubility of substances at ultra high pressure (at constant temperature) - for some substances in pressure range 1500bar - 2600bar) was used. On the contrary, the solubility of several dense gas low soluble substances increases at ultra high pressure. Usually the highly dense gas soluble substances act as an entrainer for low soluble substances. In most of the existing processes and extraction apparatus the substances which act as an entrainer (for example oils) are isolated in low pressure range (under 500bar) and therefore the low dense gas soluble substances can not be isolated on higher yields (for example carotenoids). In these cases to high solvent/feed ratios are needed and therefore such processes are not operated on commercial scale.

In our invention substances were selectively extracted in pressure range 1500bar - 2500bar, where the solubility of entrainer substances is already low and the solubility of “low” soluble substances is already high.

The additional fractionation of substances in the extract were performed by pressure and/or temperature dependent precipitation and/or by chromatographic methods incorporated in extraction plant.

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