Introduction

Most of the commercial production plants work at moderate pressures lower than 300 bars. The design pressure is limited to approximately 300 bars because the production costs per bar increase proportionally with raising pressure. From literature it is well known that with ascending pressure density as well as the dielectric constant of CO₂ are increasing thus the solubility for different components is rising. Through the change of interactions at higher pressures molecules, which are difficult to dissolve at lower pressures will be allowed to be extracted. Therefore there is a chance for extraction of high grade of explosive specialties, like fried additives and raw materials for the production of Functional Food.

New Horizons with 1000 bars

The solubility of substances in supercritical CO₂ depends on pressure and temperature. Higher pressure and thus higher density often improves the solubility of compounds. Consequently we decided to construct a pilot plant for extraction pressures up to 1000 bar to solve special substances which are not extractable with CO₂ using lower pressures. Some examples for the application of this plant are the production of Xanthohum rich extracts (Figure 1), the dehmannification of Tea or the improvement of the decaraffination of Tea.

Description of the 1000 bars pilot plant

The plant design is shown in Figure 2. The pump compresses the CO₂ to the desired pressure and the solvent is tempered to extraction conditions in the heater. The carbon-dioxide flows through the extraction vessel, inside the extraction vessel is the raw material in a basket (Figure 3). When operating with fractionating separation, the collected gas is depressurised at the PCV 1 (pressure control valve) to the separation pressure of the first separation step. Temperature adjustment (heating or cooling) follows in evaporator 1. Due to the now lower solubility parts of the dissolved substances fall out and are collected in separator 1. At the PCV 2 the gas pressure is finally reduced to the CO₂ storage pressure and the carbon-dioxide is set to the required temperature of the second separation step by evaporator 2. The substances soluble in separator 1 precipitate in separator 2. It is also possible to extract within an extraction cycle at different conditions (pressure and/or temperature) and collect the resulting extracts separately in the two separation vessels (fractionating extraction). The regenerated solvent is then liquefied in a condenser and subcooled and reentrained to the CO₂ pump. The plant is PLC-controlled allowing complete automated operation from pressurisation to depressurisation of the extractor. Furthermore all relevant measurements are recorded and logged. Thus the results are reliable and the proceeding of one extraction can be traced afterwards.

Xanthohumol extraction from hops

Hops are important for the brewing industry. They provide bitter substances, aroma components and polyphenols. Besides this, hops improve the microbiological stability.

A special polyphenol of hops is Xanthohumol. In vitro tests have shown anti-carcinogenic effects (1). Therefore it is of interest to extract Xanthohumol from hops and use this substance also in other products than beer.

Xanthohumol, an isoprenylflavonoid of the chalcon group is characterised by an unusual solubility. It is nonpolar, so that it is hardly soluble in hot water, but good in ethanol or ethan-alcohol mixtures. On the other hand nonpolar solvents like hexane can not extract Xanthohumol. With CO₂ the polyphenols including Xanthohumol are not extractable below pressures 300 bars. How changes the solubility of the Xanthohumol with rising extraction pressures?

For the extraction tests we used hop pellets and the residues from commercial CO₂-hop extraction. At the parameters of commercial CO₂-extraction polyphenols are insoluble. So the residues (spent hops) contains all the polyphenols. The spent hops were filled in the extraction basket of the 1000 bar pilot plant and percolated with carbon dioxide at different conditions.

A series of different extraction conditions showed that we are able to produce an extract containing 32 weight-% of Xanthohumol. The extraction conditions, which seem to be best, are 800 bar and 85 °C (2). The highly enriched extract is solid at room temperature.

Decyanisation of Cacao

Cacao and cacao drinks are popular natural stimulants. Cacao contains the Methylxanthines Theobromine, Theophylline and Caffeine. Many consumers have to avoid the intake of Methylxanthines according to health issues. Therefore coffee and tea were offered since several years caffeine free. Cacao and cacao products can contain up to 0.25 weight-% Theobromine and 0.20 weight-% Caffeine. Nevertheless there is no industrial process to produce a high quality decyanated cacao.

Form tests showed that supercritical carbon dioxide at a pressure of 280 bar, a temperature of 80 °C and with the addition of the entrainers water and ethanol can extract the Methylxanthines (3).

The aim of the new test series was to demonstrate what happens at extraction pressures up to 1000 bars. For the trials three different starting materials were used. Defatted cacao (fat content < 1 weight-%), cocoa cake 10/12 (fat content between 10 and 12 weight-%) and roasted cacao nibs. The extraction with dry CO₂ at 800 bars and 80 °C gives an unsatisfactory result, because the Theobromine content could be reduced only by 30 % with a flow ratio of 500 kg CO₂/cacao. Thus an economical production process is not possible.

Tests runs with water as entrainer could be done only with cacao nibs, because defatted cacao and cacao cake 10/12 absorb water, swell and finally block the CO₂ flow.

Decaffeination of Tea

The decaffeination of tea and coffee is a well known process. In case of coffee usually the green beans are treated. Caffeine is reduced to the desired level. Only after this processing step the beans are roasted to develop flavour and aroma components. Sensory nearly no difference can be detected between regular and decaffeinated Coffee.

Opposite to the decaffeination of coffee the green or black tea ready for consumption is decaffeinated. Therefore the excellence of the extraction step is determining the quality of the final product. Especially long exposition of the tea leaf to warm and wet solvent degrades its quality considerably.

Today mainly supercritical carbon dioxide is used as solvent applying pressures between 200 and 300 bars and temperature between 10 and 80 °C. At these extraction conditions the antiancerogenic polyphenols Epicatechin-gallate and Epicatechins-gallate are not soluble.

Because of limited solubility of caffeine in CO₂ the process needs long time. Consequently the quality is affected. The expert skilled in the art would apply higher extraction pressures expecting shorter extraction times but simultaneously a loss of aroma compounds.

The intension of the test series was to make a comparison of the quality between teas produced with pressures of 500 and 1000 bars and by the commercial extraction.

The findings of the experiment with higher pressures have been:

- The extraction time could be shortened to approx. one half of the time.
- The antiancerogenic polyphenols are not soluble up to pressures of 1000 bar.
- Sensory evaluation demonstrated even higher quality of the infusion (opposite to the expectation).

Conclusion

The extraction with pressures up to 1000 bar offers possibilities for the production of new substances and the improvement of already existing industrial processes as the test series shown. Further fields of application for higher pressure are the selective extraction of natural pigments and the winning or the enrichment of carotenoids from plant material.

References