

Experiments, Modelling and Scale-up for Supercritical Extraction from Plants

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INTRODUCTION

The extraction of natural products with supercritical carbon dioxide has been introduced on industrial scale in the last decades and the number of industrial plants is increasing. It is therefore important to develop and apply procedures for optimisation of the extraction process, using preferably phenomenological models. The models should describe three aspects of the extraction: phase equilibrium, mass transfer, and flow pattern of the solvent in the extractor.

Technical design of industrial plant for supercritical extraction based on pilot plant experiments in the Separex company is described in congress contribution [1]. The pilot plant is used first to determine the optimal extraction conditions scanning different pressures, temperatures and solvents, and then to obtain thermodynamic and kinetic data. The appropriate extrapolation method for scale-up depends on the mechanism controlling the extraction, which could be the solubility of the extract in the fluid, internal diffusion in the extracted material, or their combination. If the extraction rate is limited by the solubility or thermodynamic equilibrium between the solid and fluid phases, the solvent mass required for the extraction from unit mass of the feed (extracted plant) should be kept constant in small and large equipment. When the extraction is controlled by internal diffusion, the mass ratio of flow rate to feed, which is proportional to solvent residence time in the extraction bed, should be kept constant, claim the authors [1]. When both diffusion and solubility are important, a versatile mathematical model for extraction is solved numerically. Thermodynamic equilibrium is described in the model either by the solubility of the extract or by a linear or Langmuir type equilibrium that is known from desorption/adsorption. Linear driving force approximation is used for the external and internal diffusion, and the axial dispersion is simulated dividing the extractor axially into a series of ideal mixers.

The design procedure is illustrated on vegetable oil extraction from ground seeds [1]. Two extraction periods are distinguished in the model. First, the easily extractable fraction of total oil is extracted and the solvent flowing out of the extractor is completely saturated with oil, which solubility in CO₂ under given pressure and temperature was measured separately. The second period is controlled by internal diffusion and the internal diffusion coefficient is the same for any size of extractor. Thus, only two model parameters have to be determined from the pilot plant extraction, the fraction of easily extractable solute and the internal diffusion coefficient.

In this contribution, the basic ideas are identical with the cited work but the model is more detailed and extended by the findings published in the last decade. A procedure for laboratory/pilot plant extraction data collection and scale-up is proposed.

EXTRACTION PROCESS

The extractor is a high-pressure cylindrical shape vessel usually in vertically position. The solvent flows through a fixed bed formed by solid particles of pretreated (dried, ground) botanic material and is gradually saturated with extracted substances. Like any extraction from fixed bed of solid particles to a stream of solvent, the process has three aspects: phase equilibrium, mass transfer and flow pattern. Their special features are given by the properties of supercritical solvents, particularly their low viscosity and in the case of carbon dioxide also its relatively low solvent power, and by very low permeability of dry plant tissues.

Phase equilibrium

By far the most popular supercritical solvent in the extraction from plants is carbon dioxide. Its non-toxicity and non-flammability, relatively low critical point, and low cost make it a perfect substitute for organic solvents. It is a non-polar solvent; to dissolve polar substances, it should be modified by addition of small amounts of conventional solvents. Water, that is always present in plants, even dry, serves to a certain extent as a natural modifier. The solvent power of supercritical solvents strongly depends on pressure and temperature, but even at optimum extraction conditions the solubility of extracts in supercritical CO₂ (SC-CO₂) rarely exceeds a few mass per cent. Moreover, solute-matrix interaction exists; at least a part of extract does not dissolve freely but is bound (adsorbed or absorbed) on plant matrix. **Figure 1**, where the fluid phase concentration y^+ is plotted against the solid phase concentration x^+ , shows a simple simulation of such equilibrium proposed by Perrut et al. [2]. If the initial concentration in the extracted material is sufficiently high, the equilibrium fluid phase concentration equals to the solubility y_s until the solid phase concentration decreases x_t . The rest of solute interacts with matrix and the equilibrium is characterised by linear relationship with partition coefficient K . If the extraction starts from solid phase concentration lower than x_t , the linear equilibrium relationship applies from the very beginning.

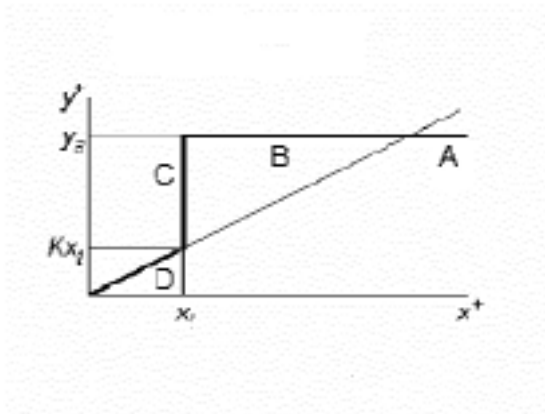


Figure 1. Phase equilibrium [2].



Figure 2. a) Particle of ground seed; b) Piece of leaf with glandular trichomes

Mass transfer

The solute is deposited in the plant in various cavities called usually “cells” in the extraction models distinguishing between broken and intact cells [3, 4]. **Figure 2** shows

two plant particles containing each two extract fractions, distinguished with respect to their location. In case a), the grey region close to particle surface indicates oil-containing cells whose walls were mechanically damaged by grinding; in the dark region inside the particle the cells are intact. In case b), most of the essential oil extracted from leaves is easily accessible as it is deposited mainly in fragile glandular trichomes on the leaf surface. Contrary to the extraction with organic solvents where the cell tissue swells and becomes more permeable, the extraction with SC-CO₂ is a “dry” process where the permeability of plant tissue remains low. The difference in external mass transfer coefficient k_f , characterising in the models the mass transfer from broken cells, and the internal mass transfer coefficient k_s , characterising the mass transfer from intact cells, is therefore very large, several orders of magnitude.

Flow patterns

Figure 3 shows different solvent flow patterns in extraction bed. The maximum extraction rate is obtained in the extractor with plug flow, and many published sets of extraction data suggest that deviations from the optimal flow pattern occur quite often. Very short extraction beds are better simulated as ideal mixers.

In the longer extraction beds, the deviations from plug flow are caused not only by the well known axial and radial dispersion but very often also by natural convection to which due to their low kinematic viscosity the supercritical fluids are extremely prone. It is induced at lower flow rates by solvent density differences caused by the differences in local solute concentrations. Its occurrence depends also on the direction of solvent flow through extraction bed, as Beutler et al. discovered in their experiments. [5, 6] When the flow was from the top of the extractor to its bottom, extraction yields from plants were higher than in the case of opposite flow direction. The extractor with natural convection can be simulated as ideal mixer.

Channelling, which develops when the solvent under pressure starts flowing through a compact layer of sticky particles, affects the extractor performance most negatively. The solvent quickly escapes from the extractor and mass transfer from the bulk of the extraction bed to the channels is very slow. The extraction with channelling can be simulated as ideal mixer with substantially reduced external mass transfer coefficient k_f [4]. To prevent channelling, the particle size should not be less than 0.4 mm, and a good solvent flow distributor should be used to ensure uniform flow at the solvent inlet to extraction bed.

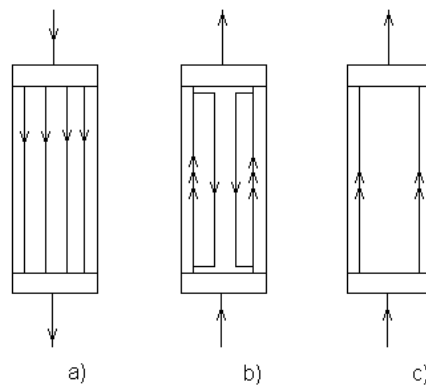


Figure 3. Solvent flow patterns. a) Plug flow; b) Ideal mixer; c) Channelling.

TWO EXTRACTION PERIODS

The extraction is characterised by extraction curve where the extraction yield e (kg extract/kg feed) is plotted against the mass of solvent passed through the extractor per unit mass of feed q (kg CO₂/kg feed). **Figure 4** shows extraction curve typical for the extraction of essential oils, which is formed by the straight line in the first period and by the bowed curve in the second extraction period; both sections are smoothly connected by a short transition section. The curves for vegetable oil extraction from seeds look different; they exhibit a sharp switch to the second, slow extraction period without any transition section.

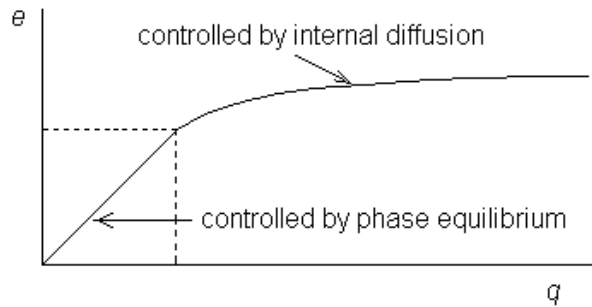


Figure 4. Extraction curve.

In the second period that is controlled solely by internal diffusion the extraction curve is

$$e = x_u [1 - C_1 \exp(-t/t_s)], \quad t_s = l_s/k_s \quad (1)$$

where x_u (kg/kg) is the initial extract content in the feed, C_1 is a constant dependent on the initial fraction of easily accessible solvent, t_s (min) is the characteristic diffusion time, l_s is the characteristic dimension of the particle region with intact cells, and k_s is the internal mass transfer coefficient.

The extraction curves for the first extraction period were calculated on the assumption of negligible external mass transfer resistance are shown in **Figure 5**. They depend both on

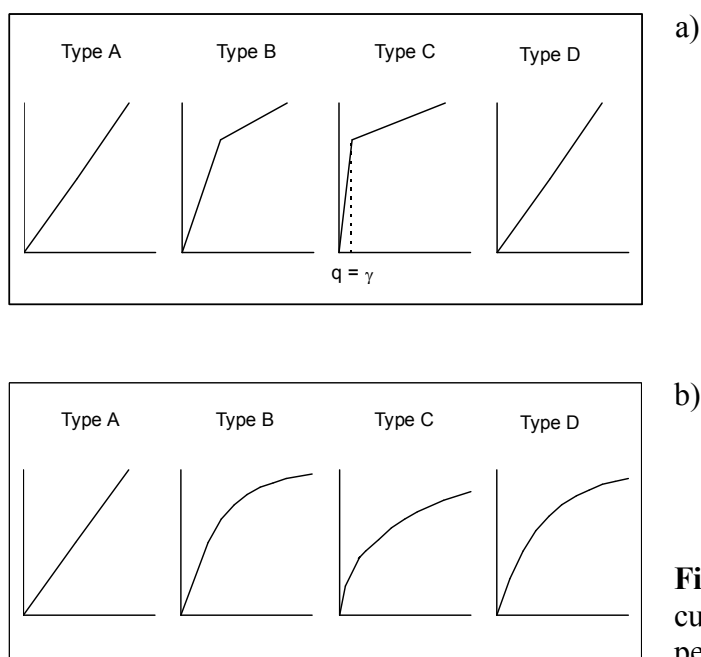


Figure 5. Equilibrium extraction curves $e = e(q)$ in the first extraction period. a) Plug flow; b) Ideal mixer.

the solvent flow pattern and on the initial phase equilibrium in the extractor, whose position in the equilibrium relationship is indicated in **Figure 1** by letters A-D. The initial slope of extraction curves of type A and B is equal to the solubility y_s . For the curves of type C starting at transition solid phase concentration x_t , however, the initial slope is lower than y_s . This type of extraction curves is recognized according to the fast switch to slower extraction as soon as the solvent filling initially the extraction bed is washed out. The initial slope of the curves of type D depends on the mass ratio of the solvent filling the void space in the extraction bed to feed γ , the fraction of easily accessible extract r , and K , x_u :

$$de/dq|_{t=0, \text{equilib}} = \frac{Kx_u}{1 + \gamma K/r} \quad (2)$$

If the solvent flows in plug flow, the slope of the second section of extraction curves of types B and C is equal to Kx_t . The effect of external mass transfer resistance on the slope is

$$de/dq|_{t=0} = de/dq|_{t=0, \text{equilib}} [1 - \exp(-1/\Theta)] \quad (3)$$

Plug flow is recommended for the evaluation of model parameter from two separate parts of extraction curve because the changes in the shape of extraction curves measured for ideal mixer are less “readable” due to the smooth transitions between the sections. More details on the simplified model for two extraction periods and on the complete model for supercritical extraction with numerical solution, be found elsewhere [4], including explanation how the mass transfer resistance Θ inversely proportional to k_f is calculated.

To distinguish whether the extraction is equilibrium-controlled or diffusion-controlled, several extraction runs are performed at identical conditions except for the varied solvent residence time t , and the extraction yields are plotted against the extraction time and the solvent-to-feed ratio, q , as in **Figure 6**. If the extraction curves overlap in the graph $e = e(t)$, the extraction is controlled solely by diffusion. If they overlap in the graph $e = e(q)$, it is controlled solely by equilibrium like in Figure 6 where the extraction is of type C, the flow is close to plug flow and the decrease in extraction rate occurs when all free solute has been exhausted and the extract adsorbed on matrix starts being extracted. At the transition to the diffusion controlled period, the extraction curves $e = e(q)$ would start following different trajectories.

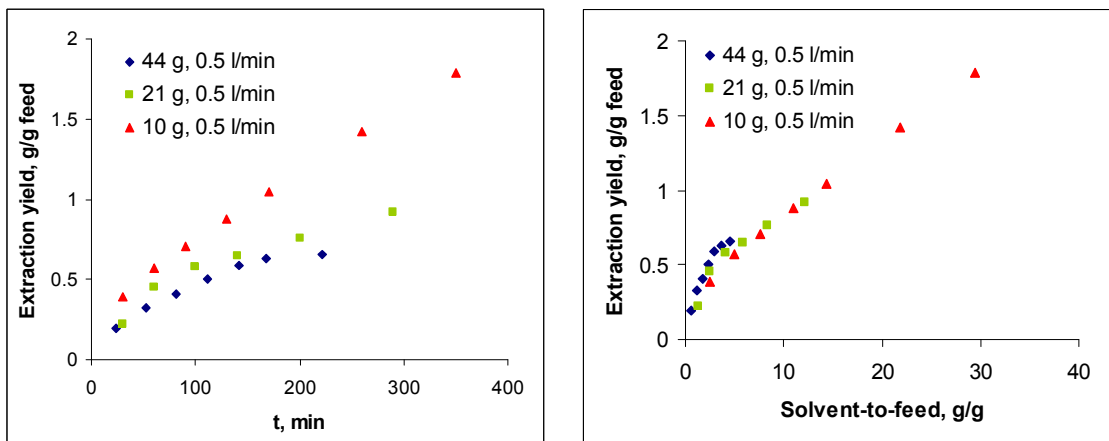
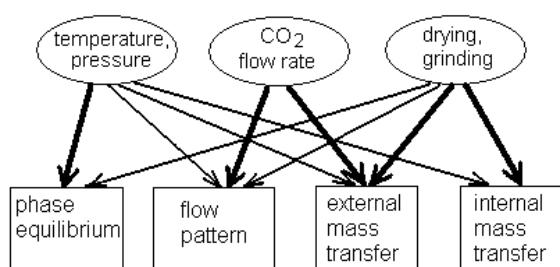


Figure 6. Peppermint oil extraction from leaves at 40 °C and 10 MPa.

SMALL-SCALE EXPERIMENT AND SCALE-UP

The scheme in **Figure 7** indicates how individual extraction conditions affect the process; the thick lines mark the strongest influence. It is evident that the extraction curves measured in small laboratory equipment enable us to adjust most of the model parameters for large equipment. After the optimisation of extraction temperature and pressure and plant material pre-treatment, these conditions are maintained constant and therefore the phase equilibrium and the internal mass transfer coefficient do not vary, too. The phase equilibrium parameters are established under these conditions from extraction runs carried out with sufficiently long solvent residence times. The internal mass transfer characteristics is evaluated from the data measured in the second extraction period and the fraction of easily accessible extract is related to the extraction yield at the crossing point of the curves fitted to the data in the first and second extraction period. Next, the extraction runs with



shorter solvent residence times and with different flow rates are carried out in order to provide information on the external mass transfer coefficient and its dependence on the solvent velocity in extraction bed. It is recommended to maintain the flow pattern as close as possible to plug flow for all these measurements.

Figure 7. The effects of extraction conditions on equilibrium and kinetics.

Extraction yield in the large-scale extractor is then calculated for different plant feeds, solvent flow rates, and flow patterns. The real flow pattern, however, is not quite safely predicted. Comparison of the plug flow model prediction with extraction data measured in the large-scale extractor then indicates how far the extractor performance is from the ideal case and whether any measures providing a better flow distribution in the large-scale extraction bed should be taken.

ACKNOWLEDGEMENTS

The authors wish to thank the Grant Agency of the Czech Republic (203/04/0120) for support of this work.

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