Modelling of Supercritical Fluid Extraction of Plant Materials

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Several applications of supercritical fluid extraction are already well known. For efficient and economical applications it is necessary to know the effects of sample characteristics (moisture content, oil content, particle size, density), packed column characteristics (specific void fraction in bed, specific surface, load volume), operation parameters (residence time, pressure, temperature, solvent flow rate), and their optimal values, because they can highly affect the quality and quantity of the products. To determine the optimal values of these parameters process modelling is a useful tool.

In various plant materials the amount and composition of soluble materials differ considerably. Generally, the yield curves obtained by supercritical fluid extraction can be divided into two parts. The first, linear part is proportional to the solubility, while the extraction velocity in the second part is much slower because it is determined by internal diffusion. In the latter case the extraction velocity (gradient of the curve) decreases quickly since it is more difficult to obtain soluble components from closed inner cells. The ratio of these parts strongly depends on characteristics of the raw material and extraction conditions. Extracting a raw material with low soluble material content (e.g. marigold), only a small fraction of the soluble material is on the surface of the particles, so the first linear part of the extraction curve is negligible, while extracting raw material with medium or high oil content (e.g. paprika, corn gem) the two different extraction rate parts can be observed.

Mathematical models, based on mass balance, allow the calculation of yield in function of time. In this work two different models were applied.

Extracting plants containing low amount of soluble material the extraction curves can be well described by the Brunner equation [1], which is a two parameter, simple model based on first order kinetics. The other applied model was the more complex Sovová's model [2] that considers many parameters, and can be widely used independently from the initial soluble material content.

The Sovová model contains four parameters (Q and S – dimensionless model parameters, τ - minimal extraction time, q – soluble fraction on the surface of the particles). These parameters can be expressed by physical parameters which depend on extraction conditions and packed column characteristics. The first step in modelling is to determine the independent parameters. Some characteristics of raw materials and packed columns were determined using different simple measuring methods (sieving, air pycnometry, traditional solvent Soxhlet extraction). Furthermore, simple empirical equations were used to determine as many other parameters (density, viscosity, solubility, diffusion coefficient, mass transfer coefficient in the fluid phase) as possible. From the parameters obtained this way Q and τ model parameters can be calculated.

The rest of the model parameters (S, q) were determined by curve fitting. For fitting yield curves a computer program was developed. The mass transfer coefficient in the solid phase can be calculated from S dimensionless model parameter.

Present study shows the effects of pressure, solvent flow rate and extractor size on the model parameters.

The yield and the necessary extraction time depend considerably on the solubility of components in supercritical solvents, which can be modified within a wide range by changing the extraction pressure and / or extraction temperature. The effect of extraction pressure (250 – 450 bar) was shown by evaluation of marigold extraction curves. The extraction temperature was 40°C during these experiments, and both models were applied. Below 350 bar, as the rise in pressure increases the solubility of components in carbon dioxide, the efficiency of the extraction improves with the application of higher pressures. By increasing the pressure the mass transfer coefficient in the solid phase (k_f) increased, and the model parameter (τ) indicating the minimal extraction time decreased significantly. While above 350 bar there was no significant effect of pressure in the range investigated.

When choosing the solvent flow rate, we have to consider the transport capacity of the pump, the rate of dissolution, and the necessary residence time for reaching the apparent solubility. To examine the effect of solvent flow on the extraction process, pre-pressed corn germ was extracted applying different flow velocities ($1.6 \cdot 10^{-4}$ – $4.1 \cdot 10^{-4}$ m/s). The extraction pressure and temperature were 450 bar and 40°C, respectively. The mass transfer coefficient in the fluid phase increased, while with the increase in solvent flow rate the minimal extraction time significantly decreased.

To explore how the extractor size influences these processes, the same paprika samples were extracted using equipment with different extraction volumes (5 L, 80 L), while the packed column geometry (length / diameter), the solvent ratio (solvent flow rate / raw material) and the extraction time were kept at similar values. The extraction pressure and temperature were 300 bar and 50°C, respectively. The Sovová's model parameters were examined in both cases and a much lower value of q model parameter (soluble material fraction in the surface of the particles) could be observed in the 80 L extractor. As the same samples were processed, a decrease in the soluble material fraction on the surface means a decrease in the easily accessible material fraction, which can be explained by changes in the packed column structure and fluid flow (raw material consistency, solvent distribution, creation of solvent channels).

Before launching a new technology, we can use modelling to determine the yield and remainder concentration curves to be expected, which are necessary for the realization of economical operation. In this work the relationship were presented among several physical parameters (characteristics of sample and packed column, extraction conditions), and the model parameters of the process. Using this modelling method the effects of some physical parameters can be approximated without performing experiments, which reduces the number of usually expensive test experiments.

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