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# Differences in CO<sub>2</sub> extraction of vegetable oils, essential oils, and minor components from plants

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## Abstract

Significant progress in understanding the phenomena that control supercritical fluid extraction from plants was made in the last years and is reflected in the literature. Combination of chemical engineering approach and botanical knowledge has appeared to be fruitful for the choice of extraction model and even for the prediction of extraction kinetics. This contribution refers to the papers utilizing knowledge of plant microstructure and location of extracted substances together with extraction equilibrium and attempts to specify the differences among extraction kinetics of vegetable oils, essential oils, and other substances. The most abundant substances like vegetable oils in seeds can be regarded in first approximation as non-interacting with plant matrix, in contrast to the minor components whose equilibrium concentration in CO<sub>2</sub> is affected by their adsorption on matrix and often also by co-extracted substances.

Keywords: supercritical fluid extraction; plants; kinetics; microstructure; equilibrium

## 1. Introduction

The supercritical fluid extraction (SFE) from plants is a mild, clean, and environmentally friendly separation method. It has been applied on industrial scale already for decades. After the first facilities for the extraction of hops aroma and caffeine from green coffee beans, a number of new applications has appeared [1]. Besides caffeine from tea, other biologically active substances for nutrition and cosmetic products are obtained from various herbs and plants. Moreover, unwanted substances are removed from vegetable materials like rice and cork. The SFE from plants is based on the solvent power of supercritical (pressurized) carbon dioxide, which after the pressure reduction diminishes and the extract precipitates. The extraction takes place semi-continuously, the solvent flows through a packed bed of plant particles in a cylindrical extractor and after the separation from extract in another vessel it is pressurized again and returns to the extractor. CO<sub>2</sub> as a non-polar solvent extracts from vegetable materials mainly fatty oils and essential oils, cuticular waxes, carotenoids and similar substances. A polar modifier like water, which is present even in dry plants, or ethanol added to CO<sub>2</sub> enables also extraction of polar substances.

The extraction kinetics depends on many variables to be optimized: extraction pressure and temperature in the region above the CO<sub>2</sub> critical point 7.4 MPa and 31.1 °C, which determine the solubility, the solvent flow rate and its flow pattern, the content of extract in plant and the feed of plant material, and also the plant pre-treatment by drying and milling or cutting. Results of SFE of hundreds of plants examined in laboratories have been published. However, what decides whether to realize the process industrially are the estimates of production cost [2]. For such estimation, a mathematical model is necessary to scale-up the results from laboratory equipment and to optimize process variables.

Models for kinetics of SFE from plants have been developed for several decades, too; the literature contains tens of them. Particularly, the description of internal mass transfer in plant

particles is due to different morphology of plants and their parts extremely variable. The recently developed models based on knowledge of microstructure of extracted particles, enabled by studying their enlarged images obtained by scanning electron microscope (SEM), represent significant progress.

This paper aims to draw attention to these detailed models for mass transfer from plants and to show what differences in extraction kinetics arise from different location of vegetable and essential oils in plant particles. The extraction of minor extract components is discussed, too.

## 2. Mass balance equations

Phenomenological models for the semi-continuous extraction are derived from mass balance of extract in a volume element of extraction bed. They have a form of differential equations for extract concentration in plant particles and in the fluid phase among them in dependence on time,  $t$ , and space [3]. The rate of change of concentration in the fluid phase is equal to the difference between the inflow and outflow from the element plus mass transfer rate from the particles, which is equal to the rate of extract decay in the particles.

The extraction kinetics is affected by three factors: the equilibrium concentration of extract in the fluid phase, the mass transfer resistance, and the flow pattern in the extractor. Out of them, the flow pattern is defined already by the form of mass balance equation for the fluid phase. The fluid phase concentration is usually supposed to vary only in the axial direction. The equation contains a term for axial dispersion, which coefficient is estimated from a correlation of dimensionless numbers. The effect of axial dispersion is negligible at large Peclet numbers, it is in long extractors and for large flow velocities; the term for axial dispersion is then deleted from the equation and a plug flow regime is simulated. On the contrary, the fluid phase mixing in short extractors is so intensive that they can be regarded as ideal mixers and ordinary differential equations are used instead of the partial differential equations. Axial dispersion can be modeled also by representing the extractor as a series of ideal mixers; a set of ordinary differential equations is obtained.

The mass balance equations are integrated to obtain time-dependent concentration profiles. The extraction yield,  $e$  (kg/kg plant), is calculated from the outlet concentration  $y_{out}$  (kg/kg  $CO_2$ ):

$$e = \int_0^t q^t y_{out} dt \quad (1)$$

where the specific flow rate,  $q^t$  (kg  $CO_2$ /kg plant 's), is the mass flow rate over the feed.

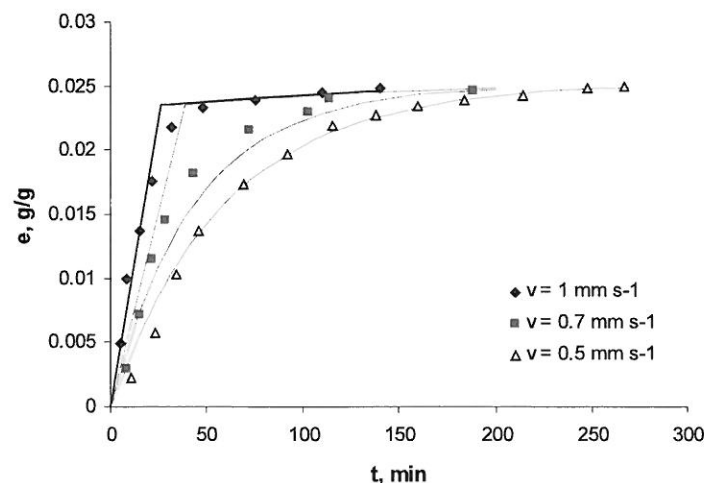


Fig. 1. Extraction yield of essential oil from pennyroyal leaves under different solvent flow velocities  $v$  [4]. Straight lines: plug flow model, curved lines: lumped parameter model.

The dependence of flow pattern on flow velocity is apparent in Fig. 1. The experimental data on SFE of pennyroyal oil taken from the literature [4] are marked by symbols and the extraction curves are calculated using the mass balance equations for plug flow and for ideal mixer (lumped parameter model). The effect of axial dispersion is negligible at the maximum flow velocity; the experimental extraction curve measured at medium velocity is between the curve for plug flow and the curve for a mixer, while at the lowest flow velocity we can suppose that the fluid phase in the extractor was perfectly mixed. In this case, the mixing probably arises from natural convection, as the solution density increases upwards, in the direction of mean flow and thus of increasing concentration.

The term for mass transfer rate contains equilibrium fluid phase concentration and mass transfer coefficients. The equilibrium fluid phase concentration can be determined experimentally when the flow pattern is not far from the plug flow and the solvent residence time in the extraction bed is long enough to obtain saturated solution at the extractor outlet. When there is no extract-matrix interaction, the equilibrium outlet concentration is equal to the solubility of extract in the solvent. When, however, the extract is adsorbed on plant matrix or absorbed in a liquid component of plant particles, its fluid phase equilibrium concentration is lower than its solubility and depends on its concentration in the matrix or liquid. Different relationships are used in SFE models for this dependence but the simplest one is the linear equilibrium characterized by partition coefficient [5].

The external mass transfer coefficient in supercritical fluids is relatively large and therefore the external mass transfer resistance affects the extraction yield only marginally. The coefficient is usually estimated from a correlation [3].

The internal mass transfer in the particles is characterized by effective diffusivity or by internal mass transfer coefficient. Different concepts are used [3]: diffusion models with extract diffusing to particle surface where the interface is located, desorption models for porous particles where the solid-fluid interface is on the pore walls and the extract is desorbed into the solvent filling the pores, and shrinking core models for spherical particles with pores initially completely filled with extract; the extract-solvent interface is in the pores on the core surface and as the amount of extract in the particles decreases, the pores are gradually filled with the fluid phase and the distance between the surface of the shrinking core and particle surface, equal to the diffusion path length, extends. The extraction according to the diffusion models can be controlled by either equilibrium, when both equilibrium fluid phase concentration and mass transfer resistance are low, or by internal diffusion under opposite conditions. For the desorption models, the calculated internal mass transfer resistance is usually low and the extraction kinetics depend mainly on the adsorption equilibrium. On the contrary, the increasing internal mass transfer resistance is regarded as controlling the kinetics in the shrinking core models. The models for SFE from porous particles are well suited for the extraction of oil from seeds after pressing, when the seed matrix is so distorted that the whole oil becomes relatively easily accessible.

The broken and intact cell models (BIC models) were developed for the SFE of oil from milled seeds. They distinguish between the region close to particle surface where the walls of cells were distorted by milling and the particle core with intact cells [6]. The “cells” are cavities containing the extract, in contrast to biological cells. Due to the low permeability of cell walls there is a large difference between the extraction rates from open and intact cells, as shown in Fig. 2 where the extraction yield  $e$  (kg/kg plant) is plotted against the extraction time  $t$ . The extraction yield in the first section of the curve is matched by a straight line

$$e = (e_1/t_1)t = q\gamma_{\text{out}} \quad (2)$$

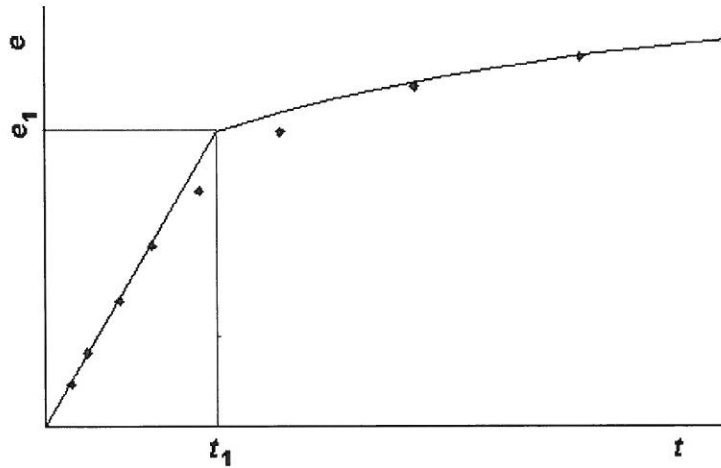


Fig. 2. Experimental extraction yields modeled by eq. (2) in the first section and by eq. (3) in the second section.

where  $q$  (kg CO<sub>2</sub>/kg plant) is the solvent-to-feed ratio. The second section, where the extraction yield asymptotically approaches the initial content of extract in the plant  $x_u$  (kg/kg plant), is modeled by the curve

$$e = x_u - C \exp(-t/t_2) \quad (3)$$

with constant  $C$ , related to the fraction of oil in intact cells, and with time constant  $t_2$ . The crossing point of both curves ( $t_1, e_1$ ) and the time constant  $t_2$  will serve in this paper to characterize the extraction kinetics according to the detailed models that take into account the particle microstructure. In the simplest case, the slope of the first part of extraction curve is equal to the product of solubility and specific flow rate, while the time constant in the second part of the curve depends only on the internal mass transfer resistance and is indirectly proportional to the second power of characteristic particle dimension.

### 3. Examination of SFE *via* the models on the micro-scale

Scanning electron microscope (SEM) images of large details of plant particles before and after the extraction give insight into the mass transfer process and enable new and more precise formulation of the mass transfer term in the mass balance equations of SFE models. The SEM images of surfaces of coriander and grape seeds [7], sunflower seed [8], and amaranth seed [9], for example, can be found in the papers on models for SFE, as well as the images of aromatic herbs like oregano bracts [10, 11], mint leaf [12], marigold flower [13,14], chamomile flower [14], fennel fruit [14], valerian root [15, 16], wild thyme leaf [16], celery fruit [16], nutmeg [16], or leaf of *Persea indica* [17].

#### 3.1. Vegetable oils from seeds

As the SEM images of surface of different seed particles show, the surface of seed particles consists of a net of open cells that initially contain oil and after the extraction they are almost empty except for small corns of starch, which is insoluble in CO<sub>2</sub>. A typical cell size is 20-30 nm. Reverchon and Marrone [7] applied the BIC model for SFE from spherical particles and estimated from the volume of the layer of open cells what part of oil was initially in open



cells; however, the experimental data indicate that the real fraction of easily accessible oil was higher than this estimate and the results of calculation are therefore not quite satisfactory.

Fiori et al. [18] published a new model for the extraction of oil from spherical particles (Fig. 3). The extraction from the outer layer (outer shell) of open cells is retarded only by a small external mass transfer resistance. When the outer shell has been emptied of oil, the oil from the second shell starts being extracted; the mass transfer resistance is now equal to the sum of outer resistance plus a much higher resistance of the cell wall. When the second shell has been emptied of oil (this situation is sketched in the figure), the oil from the third shell starts diffusing through two cell walls. Thus, the extraction continues with gradually increasing internal mass transfer resistance, while the equilibrium fluid phase concentration remains equal to the solubility. Once the mass transfer coefficient between the shells is determined, the calculation of extraction kinetics for particles of any size is possible.

Comparison of model calculations with experimental extraction curve shows that the yield in the break of extraction curve is higher than would correspond to one shell of open cells; more probably, the cells in two outer shells are open. Perrut et al. [19] extracted oil from milled sunflower seed and observed that, after the break of extraction curve, the slow extraction was controlled by equilibrium similarly to the initial fast extraction. In this case, the outlet concentration  $y_{out}$  was initially equal to the solubility of oil in  $CO_2$  and then the oil adsorbed on plant matrix was extracted. The plant tissue was evidently damaged by milling to such extent that practically all cells were open.

The microstructure-based model [18] enables us to predict the changes in extraction rate with the changes in extraction conditions. The yield in the crossing point is independent of pressure, temperature, or the flow rate; it depends on particle size. For larger particles the overall number of shells increases, and the fraction of oil that is easily accessible in the outer shell or shells therefore decreases. The time constant in the second part of extraction curve,  $t_2$ , will increase due to the larger number of shells. When the specific interfacial area of larger particles is still sufficient for saturation at the extractor outlet, the slope of the initial part of extraction curve is not affected by the increase in particle size. It is, however, directly proportional to the flow rate and to the solubility, which is controlled by extraction pressure and temperature.

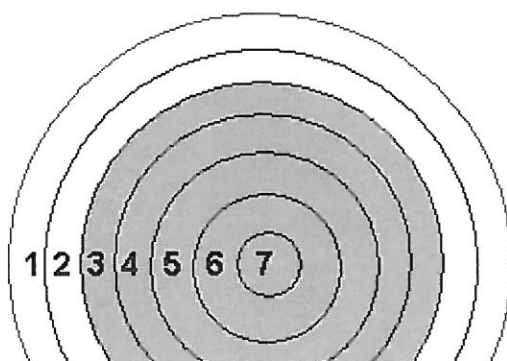


Fig. 3. Model for SFE of oil from spherical particles of milled seed. The oil from the next shell starts being extracted after the previous shell has been emptied of oil.

### 3.2. Essential oils extracted from different plants

When Reis-Vasco et al. [4] extracted essential oil from leaves of pennyroyal, they observed a break on extraction curve similar to the break typical for the SFE of vegetable oils from seeds.

They knew that most of essential oil was in the glands on the leaf surface and therefore they proposed a model of BIC type, with 70 % of essential oil on the surface, extracted without any mass transfer resistance, and the rest of oil extracted slower, controlled by internal mass transfer resistance. Gaspar et al. [11] further simplified the BIC model in order to model the kinetics of the SFE from oregano leaves: they assumed that all easily accessible essential oil on the surface was dissolved during the static extraction, before the solution starts flowing out of the extractor at  $t = 0$ . A more detailed examination of SFE of essential oil from various types of glands was undertaken by Zizovic and colleagues in the group of Professor Skala.

### 3.2.1. SFE from glandular trichomes

Essential oils in the plants of Lamiaceae family (thyme, basil, oregano, marjoram, peppermint and others) are found in glandular trichomes on the surface of leaves and other parts. Zizovic et al. [12] analyzed the SEM images of the surface with glandular trichomes before and after the extraction and related them to the shape of corresponding extraction curves. One part of trichomes disrupted already before the extraction, during the milling. The second group was intact at the beginning of extraction but these trichomes disrupted after a certain time of exposure to supercritical  $\text{CO}_2$  which diffused through the membrane of trichomes, was absorbed into the essential oil and thus increased the volume of trichomes and stretched its membrane (Fig.4). The third group of trichomes remained intact even after the exposure to  $\text{CO}_2$ . While the extraction from disrupted trichomes was fast, the extraction from intact trichomes was controlled by diffusion through the membrane. The expression for mass transfer rate in the mass balance equations thus consists of three terms.

The detailed model takes into account the initial size of glandular trichomes; their specific number is calculated from the essential oil content in plant and the volume of one trichome. The numbers of trichomes disrupted during the milling, after the exposure to  $\text{CO}_2$  and of intact trichomes is calculated from their experimentally determined mutual ratios. The time of exposure necessary for the disruption is measured, too. This time was regarded as a constant number in the first version of the model, in the improved version a distribution of disruption times was considered [16].

To express the behavior of the detailed model using the simple BIC model, we combine the extraction from the trichomes broken during the pretreatment and the extraction from the trichomes disrupted after the exposure to  $\text{CO}_2$  to estimate the value of  $e_1$ . Evidently, the yield of the fast extraction depends not only on the efficiency of milling but also on the pressure and temperature which affect both solubility of  $\text{CO}_2$  in essential oil and permeability of

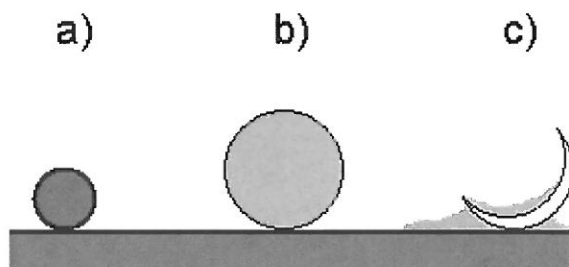


Fig. 4. Scheme of glandular trichomes (GT) of plants of Lamiaceae family. a) GT before extraction, b) increased volume of GT after absorption of  $\text{CO}_2$  that diffuses through the membrane, c) open GT after disruption of the stretched membrane.

stretched membrane. The permeability, on the other hand, determines the time constant  $t_2$ . When the properties of glandular trichomes of different Lamiaceae plants are similar, the model enables prediction of extraction kinetics for one plant with a model whose parameters were adjusted for another plant.

### 3.2.2. SFE from secretory ducts and cavities

According to the paper [14], the essential oil of the plants of Apiaceae, Asteraceae, Hipericaceae, Pinaceae, Coniferae and other families is in secretory ducts which ends are opened by milling. In contact with supercritical  $\text{CO}_2$  the volume of the solution oil+ $\text{CO}_2$  increases and a part of it covers the surface of the plant (Fig. 5). The mass transfer rate from the surface is fast, controlled by equilibrium concentration in fluid phase.

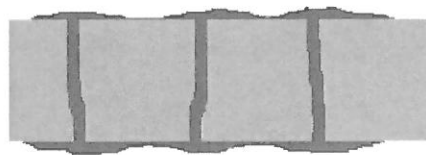


Fig. 5. Scheme of a particle with secretory ducts exposed to supercritical  $\text{CO}_2$ .

After the essential oil from the surface has been exhausted, the oil diffuses from the ducts, the interfacial area is reduced and the extraction rate is somewhat slower. Still, the mass transfer resistance is relatively small.

In comparison with the simple BIC model, the whole extraction can be the first section of extraction curve, with  $e_1$  equal to  $x_u$  (Fig. 2). The intensity of milling does not affect the extraction kinetics as the ducts are open already after a mild mechanical pretreatment of dry material.

Similar extraction kinetics is observed for the plants containing the essential oil in secretory cavities which are large enough to be disrupted by mechanical pretreatment. The plants of citrus family (Rutaceae), eucalyptus leaves, clove buds and other plants belong to this group [16] which extraction is controlled by the phase equilibrium as the mass transfer resistance is small.

### 3.2.3. SFE from secretory cells

Another type of essential oil reservoirs as secretory cells found in different plant tissues like ginger rhizome, nutmeg, cardamom, valerian root, leaf of lemongrass, bay, citronella and others [16]. The spherical cells are distributed in the whole volume of plant particle, and a part of them is broken by mechanical pretreatment. The term of the mass transfer rate in the detailed model [15] takes into account the size of the cells and describes simultaneously the faster extraction from open cells on particle surface and the extraction from intact cells inside the plant tissue. This situation is in less detail described by the simple BIC model.

The response to the changes in operation conditions is therefore same as in the model for SFE of vegetable oil from milled seeds: the extraction yield at the crossing point,  $e_1$ , depends most of all on the fraction of cells disrupted by mechanical pretreatment.



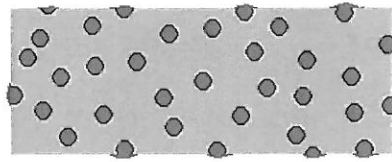


Fig. 6. Scheme of a particle with open and closed secretory cells.

### 3.3. Comparison of properties of detailed models

The properties of the above discussed microstructure-based models are summarized in Table 1. The response of the model for SFE from seeds [18] to the changes in operation conditions are applies also to the extraction from milled or cut roots, rhizomes, and for the SFE from secretory cells, it is to the extraction from materials where the extract is approximately uniformly distributed in the whole volume of the particle.

It is evident that the response of individual types of extraction to the changes in particle size and in pressure and temperature is characteristic to individual models. If possible, these operation conditions should be varied in SFE laboratory experiments to confirm the correct choice of model.

Table 1. Effect of changes of independent variables on the parameters of extraction curve

Change in variable:	Particle size ¥			Flow rate ¥			Solubility/ permeability ¥		
	$e_1$	$t_1$	$t_2$	$e_1$	$t_1$	$t_2$	$e_1$	$t_1$	$t_2$
Fatty oil from seeds [18]	§	-	¥	-	§	-	-	§	¥
Essential oil from glandular trichomes [12,16]	§	-	-	-	§	-	¥	§	¥
Essential oil from secretory ducts and cavities <sup>a</sup> [14,16]	-	-	-	-	§	-	-	§	-

<sup>a</sup>there is no break on extraction curve,  $e_1 = x_u$

### 3.4. SFE of minor components

The extracts from plants are always complex mixtures of substances. It is true also for CO<sub>2</sub> extracts, though the SFE is more selective than conventional extraction. We can expect that the kinetics of extraction of minor components will be affected by co-extracted substances, at least by major components. Therefore it is important to examine the extraction of a minor component as the extraction of minimally two components; this enables us also to model the changes in the extract composition in the course of extraction.

Very simple models of multicomponent extraction where the yields of each extract component were calculated separately and then summed were published for the SFE of essential oil, lipids, and piperine from black pepper [20], free fatty acids, triglycerides, and  $\beta$ -carotene from pressed palm oil fibres [21], and monoterpenes, sesquiterpenes and other hydrocarbons from ginger rhizome [22]. Goto et al. [23] proposed a modification of the lumped parameter model where a continuous mixture is extracted instead of one substance.

The continuous mixture is simulated as a mixture of groups of a large number of components as continuous functions of some mixture property, in this case as the Gaussian function of molecular mass. The partition coefficient is assumed to be directly proportional to the molecular mass. In the paper, kinetics of the extraction of two groups of components was predicted.

In the following models, the equilibrium of a mixture of extracted substances with the solvent was taken into account, using the separation factors that are applied in modeling the SFE of liquids in countercurrent columns. Thus, Shen et al. [24] evaluated separation factors of minor components of oil to triglycerides from the initial slopes of their extraction curves in the extraction from rice bran. Gaspar [25] examined the selectivity of individual components of volatile oil extracted from oregano bracts under different extraction conditions. Sovova et al. [26] implemented the separation factor of  $\beta$ -sitosterol to triglycerides into the model for SFE of sea buckthorn oil.

Another possibility is to link the rates of extraction with diffusion coefficients of individual extract components. Machmudah et al. [27] simulated the changes in composition of extract from nutmeg oil, distinguishing between terpene hydrocarbons with higher effective diffusivity and oxygenated terpenes and myristicin with lower effective diffusivity in order to fit the experimental data on overall extraction yield and on the changes in extract composition. Two models for multicomponent extraction were proposed by Tezel et al. [28]. The shrinking core model describes the extraction of two substances of different solubility and different effective diffusivity. The model has two shrinking cores, the inner core containing both condensed substances and the outer core with only the slower extracted compound condensed. Thus, the faster extracted component diffuses first through the outer core before it is dissolved in the solvent in the pores outside the outer core. The second model is a multicomponent desorption model for three components differing in adsorption isotherms and in effective diffusivities. The equilibrium relationship is of Langmuir type. These models were, however, not compared with experimental data.

It is evident that the attention given up to now to modeling the extraction of multicomponent mixtures is not adequate to its importance for the control of extract composition.

#### **4. Conclusions**

The models for SFE from plants are closer to reality now, when the extraction from plant microstructure is understood and described. They are not only more reliable but also assigned to concrete plant families and/or parts of plants (seed, leaf, flower, root ...). The effects of extraction conditions and of plant pretreatment on the kinetics of SFE of vegetable oils and of essential oils are well simulated by the models. Much less attention has been paid to examination of kinetics of extraction of minor extract components where the effect of co-extracted components has to be taken into account; it is a challenging task. A multicomponent equilibrium seems to be a key to its solution, at least for the initial, fast extraction, which is usually decisive in industrial applications.

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