TOWARDS A BETTER UNDERSTANDING OF SIMULATING THE MULTICOMPONENT SOLUBILITY OF NATURAL EXTRACTS IN SUPERCRITICAL CARBON DIOXIDE

S. Maharaj[*], D. R. McGaw, M.Watson, R.Skeene and B. Sellier
[*] Sharad.Maharaj@sta.uwi.edu

ABSTRACT

A number of mass transfer models have been proposed to describe the process of Supercritical Fluid Extraction. All of these models assume the essential oil/ oleoresin to be a bulked entity, whereas in practice most extracts comprise a number of compounds. In addition, they do not fully recognise the internal structure of the plant material nor do they incorporate the specific characteristics of packed bed operation. A model is presented which starts from the premise of the breakdown of the cell structure on applying the fluid under supercritical conditions. The model advocates that transfer of solutes from within the plant material to the bulk of the solvent comprises three sequential stages namely internal diffusion from within the matrix of the plant material, equilibrium at the surface of the material, followed by convective transfer from the surface to the bulk solvent phase. Relevant equations are presented which provide the basis for predicting the extraction process. The use of thermodynamic modelling of equilibrium at the surface of the material allows for the prediction of extraction of individual components at different rates, which it is known happens in practice. Superimposed on the transfer processes at the level of the particle is the recognition that concentrations of solutes within the particles and in the extracting solvent will vary with position and time in the bed of particles.

INTRODUCTION

Supercritical carbon dioxide (CO_2) solvent offers the unique facility of extracting quality-specific natural extracts from a single source of plant material owing to its tuneable solvency. The final quality of the extracts, i.e. yield and composition, also depend on a number of factors such as the geographical location and specie of the plant material used together with the process conditions such as the CO_2 density and equipment configuration.

Over the years, several mathematical models have been proposed to describe and predict extraction behaviour, the five main ones being: The Supercritical Fluid-Liquid Model, the Linear Driving Force Model, the Shrinking Core Model [1], the Broken and Intact Cells Model [2], [3] and the Broken and Intact Cells with Shrinking Core Model [4]. These models however treat the extraction as the mass transfer of a single homogenous component, when the reality is that the extraction should be regarded as the dynamic extraction of a multicomponent mixture. The analysis which follows endeavours to recognise:

1) The physical aspects of what happens to the matrix material during SFE.
2) The fact that the extracts are in fact a multicomponent mixture of a number of compounds.
3) That the process is carried out in a packed bed of material where compositions both within the solid phase and the solvent phase vary with position in the bed and with time.

MATERIALS AND METHODS

General Background to Model

Microscopic analysis of the plant material, both before and after extraction [5], has shown that the cell structure breaks down completely when subjected to the high pressures associated with SFE. Microscopic analysis of plant material, subjected to pressures ranging from 300 to 400 bar and varying times under static and dynamic extraction, were investigated. The high pressures associated with supercritical fluid extraction are thought to crush the internal cell structure of the plant material and rupture the essential oil-bearing glands.

This observation can be used as the starting point of a comprehensive model to predict the transfer of oils and oleoresins from within oil bearing materials to the supercritical fluid based on three specific transfer components:

1) Transfer from within to the surface of the plant material using the classical diffusion equation.
2) Equilibrium at the surface of the plant material, the solubility of the different components being predicted by standard thermodynamics utilising an appropriate equation of state.
3) Transfer from the surface of the plant material to the carbon dioxide phase by convection.

These relationships however relate to the transfer processes associated with extracting the oil from a single particle. In practice SFE is carried out by passing the supercritical fluid, usually carbon dioxide, through a packed bed of the material. The dynamics of transfer in packed beds, however, is such that there are changes in:

a) The concentrations of the oil in the extracting fluid as it passes up the bed
b) The concentration oils in the particles at any level within the bed with time

The proposed model therefore utilises the equations associated with 1) to 3) above to calculate mass transfer within a single layer, this then being incorporated into a layer by layer analysis which calculates the changes in compositions in individual layers with time and subsequently calculating the compositions in the supercritical fluid with both bed height and time.

Transfer from within the particle to the Surface

It is assumed that after breakdown of the internal structure of the material, the solutes are transferred from within the particle to the surface by diffusion, with the standard diffusion equation being appropriate:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial h^2}$$

Equation 1

The solution of this equation by Crank [6] is assumed to apply, with the concentration of the oil at the surface of the particle being related to the thickness of the petal/leaf and time given by:

$$x = x_o - \frac{8x_o}{\pi^2}\left[exp\left(\frac{-t\pi^2 D}{L^2}\right) + \frac{1}{9}exp\left(\frac{-9t\pi^2 D}{L^2}\right) + \frac{1}{25}exp\left(\frac{-25t\pi^2 D}{L^2}\right) + \cdots .\right]$$

Equation 2

The expansion of the equation, as given, is limited to three terms, as the contributions from the subsequent terms in the series have been determined to be negligible.

Transfer Across the Surface of the Particle

When the extracting substance reaches the surface of the particle it has to dissolve in the supercritical fluid at the surface before being transported into the bulk of the fluid. This requires a knowledge of the solubility of the substance in the extracting fluid. The simplest approach is to treat the extracting substance as a single entity, such that the partition coefficient approach, which is effectively a proportionality constant, may be applied:

$$k_p = \frac{y_s}{x_s}$$

Equation 3

It is normal however for the extracting substance to contain a range of chemicals which will have varying solubilities in the fluid. If the model is to recognise this, it is appropriate to utilise a thermodynamic approach to determine the various individual solubilities.

Using this approach, the solubility in the supercritical solvent is determined from the thermodynamic phase by equating the condensed phase and supercritical phase fugacities for the solute. Thus, the fugacity of the solute, i, in the supercritical fluid (SCF) phase is given by:

$$f_i^{SCF} = y_i \emptyset_i^{SCF} P \dots i = 1,2,3 \dots n$$

Equation 4

and that of the pure solute by:

$$f_i^{o,Solute} = P_{i,T,sublimation} \emptyset_{i,P_{i,T,sublimation}} exp \int_{P_{i,T,sublimation}}^{P} \frac{V_i^{o,Solute}}{RT} dP$$

Equation 5

Where $P_{i,T,sublimation}$ is the sublimation pressure of the pure solid at the system temperature, $V_i^{o,Solute}$, the molar volume of the pure solute and $\emptyset_{i,P_{i,T,sublimation}}$, the fugacity coefficient at the system temperature T and the sublimation pressure. The exponential term is the Poynting correction for the fugacity of a pure solute.

Using the equilibrium relationship $f_i^{SCF} = f_i^{o,Solute}$ and rearranging gives the following relationship from which the mole fraction in the fluid phase can be calculated:

$$y_i = \frac{P_{i,T,sublimation} \emptyset_{i,P_{i,T,sublimation}} exp \left(\frac{V_i^{o,Solute}(P - P_{i,T,sublimation})}{RT} \right)}{\emptyset_i^{SCF} P}$$

Equation 6

In the use of this equation, the fugacity coefficient of the solute in the supercritical phase must be determined for the system from an appropriate equation of state such as the Peng Robinson equation.

Using this approach, values of the mole fractions of all individual components in the supercritical phase at the surface of the particles can be determined.

Transfer from Surface of Particle to Supercritical Fluid
Once the components have dissolved in the supercritical fluid at the surface of the particle they will be transferred into the bulk fluid by convection. The basic equation of the two film theory

by Whitman [7] suggests that a laminar layer of fluid adjacent to the interfacial boundary is responsible for the resistance to transfer of solute. For a process where V is the volume of supercritical solvent in contact with the particles is assumed to be constant, the equation is:

$$\frac{dy}{dt} = \frac{k_f A}{V}(y_s - y)$$

Equation 7

Solving and rearranging gives:

$$y = y_s \left(1 - e^{\frac{-k_f A t}{V}} \right)$$

Equation 8

Application of this equation allows the concentration of solute components in the bulk fluid phase to be determined. Values of A and V need to be calculated from the geometry.

Packed Bed Analysis

The packed bed analysis is an extension of a similar approach which has been applied to heat transfer [8], simultaneous heat and mass transfer [9] and steam distillation [10].

In the basic analysis, in order to recognise the specific operating characteristics of a packed bed, the bed is divided into equally sized elements comprising M horizontal elements and N vertical elements as shown in Figure 1.
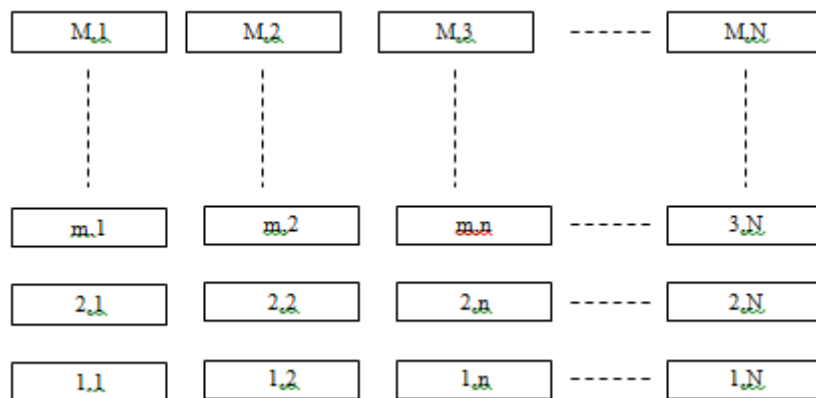

Figure 1 – Division of Extraction Bed into Horizontal and Vertical Elements

The bed is first divided into horizontal layers, each of which comprised one flower/leaf. The number of these layers governs the value of M. The bed is then further sub-divided into a series of vertical sections defined by the residence time of the solvent in the vessel, N being the number of the intervals occurring within the extraction period.

In the calculations the three basic relationships are applied to determine the concentration of the solute at the surface, in the equilibrium layer of solvent at the surface and subsequently in the bulk solvent. These are applied to each of the elements in turn and the outcomes for each element summed to predict the behaviour of the complete extraction bed.

RESULTS

A model is presented which recognises the physical effect of applying a supercritical solvent to a plant material, this being used to identify three specific resistances to the transfer of solutes from within the plant material to the solvent, namely internal transfer by diffusion, equilibrium at the surface of the plant material and transfer by convection to the bulk of the solvent. The model further recognises that extraction takes place in a packed bed of the plant material,

whereby the concentrations of the solutes in the material, and in the solvent, vary with vertical position in the bed and with time.

To date the model has only been applied using the simplified equilibrium relationship i.e. using a partition coefficient, in the extraction of the essential oil from ylang ylang and also from ginger. Comparison of the experimental result with that predicted was good, especially at the higher solvent flow rates, as shown typically in Figure 2.
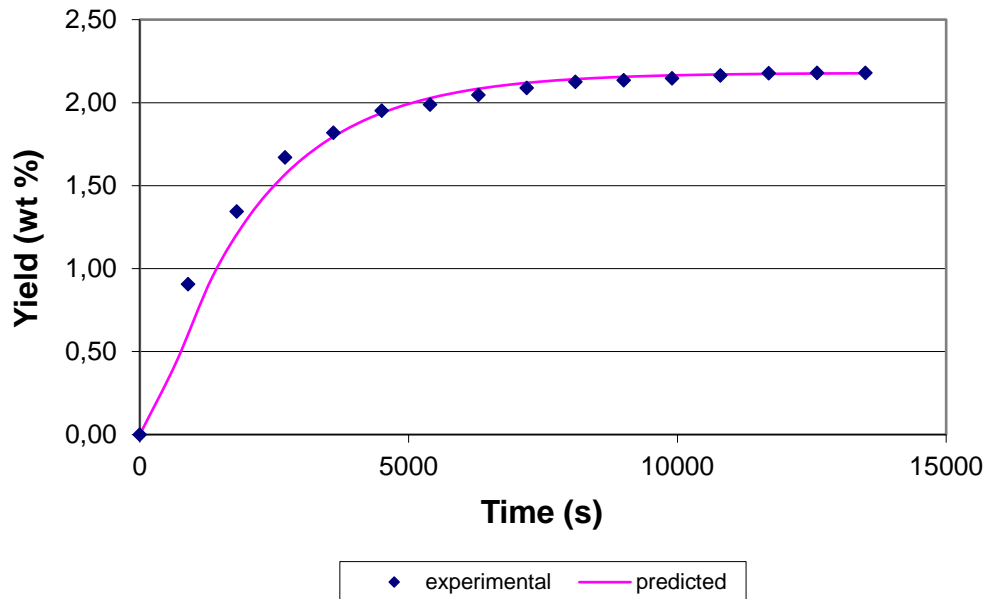
Figure 2 – Supercritical Fluid Extraction of Dried Ginger at 45°C, 120bar and 3.0L/min CO_2

CONCLUSION

The model as presented is more comprehensive than those proposed to date [1], [2], [3] and [4] and has evolved from developing an understanding of the physical situation both within the particle, its interaction with the solvent and the specific characteristics of packed bed behaviour.
The model is in the process of being applied in its entirety to specific systems to test its applicability.

REFERENCES

[1] STÜBER, F., JULIEN S. and RECASENS F., Internal Mass Transfer in Sintered Metallic Pellets Filled with Supercritical Fluid, Chemical Engineering Science Vol. 52 Issue 20, 1997, pp. 3527 - 3542
[2] SOVOVÁ, H., Rate of Vegetable Oil Extraction with Supercritical CO2 - I. Modelling of Extraction Curves, Chemical Engineering Science Vol.49 Issue 3, 1994, pp. 409 - 414
[3] SOVOVÁ, H., Mathematical Model for the Supercritical Extraction of Natural Products and Extraction Curve Evaluation, Journal of Supercritical Fluids, Vol. 33, 2005, pp. 35 – 52
[4] MARRONE, C., POLETTO M., REVERCHON E., and STASSI A., Almond Oil Extraction by Supercritical CO2: Experiments and Modelling, Chemical Engineering Science Vol. 53 No. 21, 1998, pp. 3711 – 3718

[5] WATSON, M., Supercritical Fluid Extraction of Ylang Ylang, PhD. Thesis, Department of Chemical & Process Engineering, University of the West Indies, St. Augustine, Trinidad and Tobago, 2007

[6] CRANK, J., The Mathematics of Diffusion, 2d ed., Oxford, Clarendon Press, 1975

[7] WELTY, J.R., WICKS C. E., and WILSON R. E., Fundamentals of Momentum, Heat and Mass Transfer, New York, John Wiley & Sons Inc, 1969

[8] MCGAW, D.R., Gas-Particle Heat Transfer in a Crossflow Moving Packed Bed Heat Exchanger, Powder Technology, Vol. 13, 1976, pp. 231-239

[9] MCGAW, D.R. and JAIRAM J., Drying of High Moisture Content Materials in Packed Beds, Proc. 11th International Drying Symposium (IDS'98), Halkidiki, Greece, August 19-22, Vol. b, 1998, pp. 1412-1419

[10] MAHARAJ, S., Extraction Studies with Basil, Ph.D.Thesis, Department of Chemical & Process Engineering, University of the West Indies, St. Augustine, Trinidad and Tobago, 2011