Supercritical Fluid Extraction of Vegetable Oil Seeds

N.R. BULLEY and **M. FATTORI**, Department of Bio-Resource Engineering, and
A. MEISEN, Department of Chemical Engineering, University of British Columbia
Vancouver, B.C. V6T 1W5, Canada, and **L. MOYLS**, Research Station Agriculture
Canada, Summerland, B.C. VOH 1ZO, Canada

ABSTRACT

The extraction of oil from canola seeds using supercritical carbon dioxide was investigated. The basic equations which govern the oil extraction from a bed of seeds were derived from first principles. The equations can be solved by standard numerical techniques using experimentally determined parameters for the concentration of oil in the solvent in equilibrium with seeds having a known oil content. Preliminary extraction rate data and equilibrium data are given for crushed canola seed during extraction using supercritical carbon dioxide at select temperatures and pressures. The research is directed at obtaining the basic information required for the design of continuous countercurrent extractors.

INTRODUCTION

The shortage and price increases of conventional crude oil in the early 1970s have had a major impact on Western industrialized nations. In particular, the transportation and chemical industries were severely affected since their ability to switch to alternate raw materials was extremely limited. These developments have led to renewed interest in utilizing oil-bearing plants (eg. canola, sunflower) and hydrocarbon-rich plants (eg., milkweed, guayule) as a source of raw materials.

The separation of oils and other liquid hydrocarbons from plant materials is a well developed technology. Although individual processes differ in detail, the separation is usually performed by pressing and/or hot solvent extraction. The extraction process is generally followed by purification steps to remove impurities and gum-forming compounds from the extracted oil.

Supercritical fluid extraction (SFE) is a unique extraction process which embodies several features of conventional solvent extraction while, at the same time, having important features of its own. The technique is similar to conventional solvent extraction in that the material to be extracted is "washed" from the substrate using a solvent. It differs from conventional solvent extraction because the solvent is not a liquid, but rather a gas above its critical point. In simple terms, SFE is characterized by the following attributes: (a) relatively nonvolatile hydrophobic materials can be dissolved by supercritical fluids, (b) the properties of the extraction medium can be varied within wide limits by means of pressure and temperature changes, (c) separtion of the extracted substances from the supercritical fluid can be accomplished (in whole or in part) by altering the pressure and/or the temperature of the fluid. The efficiency of the extraction depends on the temperature, pressure, contact time between the extracting fluid and the oil-bearing material, the ability of the fluid to penetrate the oil-bearing material and the solubility of the oil in the extracting fluid.

In the present paper, we are reporting our preliminary investigations on the extraction of oil from canola seeds using supercritical carbon dioxide. In addition, the basic equations which govern the oil extraction from a bed of seeds, are derived from first principles. The ultimate objective of this work is to provide information necessary for the design and operation of industrial extractors.

THEORY

To achieve high and rapid oil extraction under industrial conditions, it will probably be necessary to perform the extraction by passing the supercritical gas continuously and in countercurrent flow through the oil-bearing seeds. The design of countercurrent extractors is possible provided two types of basic information are available: (a) the equilibrium distribution of oil between the seeds and the solvent and (b) the mass transfer rate of oil from the seeds to the solvent. Although it would be better to obtain such information from a laboratory-scale countercurrent extractor, it is more convenient, experimentally, to keep the seeds stationary.

The theory is developed for the situtation where the seeds are stationary and oil-free solvent enters the extraction vessel at the top (Fig. 1). Shut-off valves are located at the top and bottom of the vessel. If the distance from the top of the bed and the bed cross-sectional area are denoted by h and A, respectively, then an oil balance on the solvent phase over an element of extractor of height δh gives:

$$\frac{\partial}{\partial t}(A\delta h\,\epsilon\rho y) = -\rho U A\frac{\partial y}{\partial h}\delta h + A_p A\delta h\,K(y^* - y) \quad [1]$$

where ϵ = voidage of the bed of seeds, ρ = density of solvent phase, y = concentration of oil in the solvent expressed as mass of oil per unit mass of solvent, U = superficial solvent velocity, A_p = surface area of seeds per unit volume of bed, K = overall mass transfer coefficient and

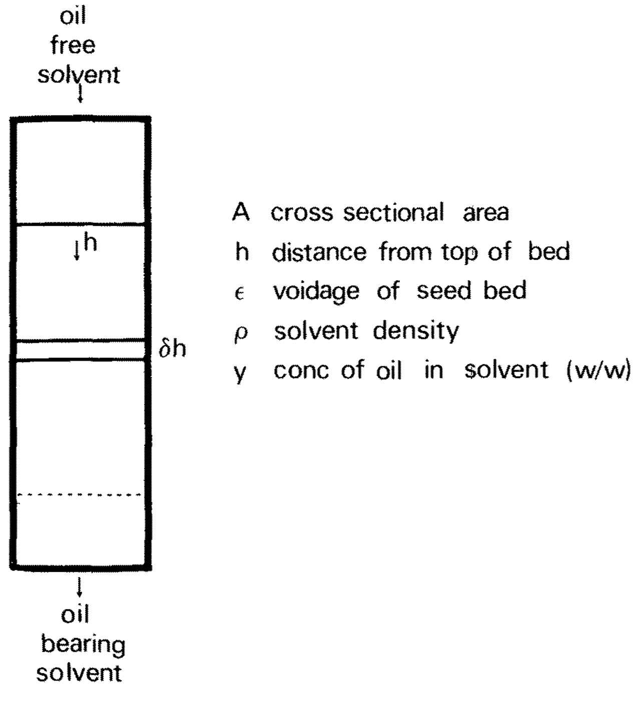

FIG. 1. Schematic diagram of the extraction vessel.

y^* = concentration of oil in the solvent which is in equilibrium with the seeds having oil concentration x.

The first term in equation 1 indicates that the extraction is an unsteady process and that the oil concentration in the solvent therefore varies with time (t) and distance (h). The equation is based on a macroscopic balance in a differential segment of the bed (1) with the assumption that the axial dispersion of oil in the solvent is negligible compared with the convective flow and that the oil concentration is small. Furthermore, it is assumed that an overall mass transfer coefficient can be used since the seed particles are small and a mean oil concentration may be assigned to them. For large particles with steep internal concentration gradients of oil, separate mass transfer coefficients should be used for inside and outside the seeds.

Equation 1 can be simplified if the solvent density and solvent flow rate are assumed to be constant, i.e.,

$$\epsilon\rho \frac{\partial y}{\partial t} = -\rho U \frac{\partial y}{\partial h} + A_p K(y^* - y) \qquad [2]$$

A similar material balance can be written for the oilseeds in an element of extractor leading to

$$(1 - \epsilon)\rho_s \frac{\partial x}{\partial t} = - A_p K(y^* - y) \qquad [3]$$

where ρ_s = density of seeds and x = oil concentration in the seeds expressed as mass of oil per unit mass of oil-free seeds.

The boundary conditions for equations 2 and 3 are:

$$t = 0 \qquad 0 \leqslant h \leqslant H \qquad x = x_o \qquad [4a]$$

$$t > 0 \qquad h = 0 \qquad y = 0 \qquad [4b]$$

where H and x_o denote the total bed height of seeds and the initial oil content of the seeds, respectively. It is also assumed that the solvent is oil-free as it enters the extractor.

Equations 2 and 3 can only be solved if the equilibrium relationship, i.e., $y^* = f\{x\}$, is known. The following subsection indicates how, in principle, this relationship may be found.

Determination of Equilibrium Relationship

By definition, y^* is the oil concentration in the solvent which is in equilibrium with the oil concentration in the seeds, x. For a given temperature and pressure, the points (x,y^*) may be found as follows: (a) Seeds with known initial weight and oil concentration (x_o) are contacted with the supercritical solvent at the desired temperature and pressure. There is no solvent flow and sufficient time is permitted to elapse for the solvent and seeds to reach equilibrium. (b) The solvent flow is started at a very low rate and the dissolved oil is collected downstream of the extractor. The solvent concentration remains constant as long as the seeds at the downstream face of the extractor retain the initial composition. The solvent concentration, y^*, is found from the mass of oil extracted (M_e) and the volume of solvent passed through the extractor. (c) Provided no breakthrough of lean solvent has occurred in step (b), the oil concentration of the seeds in the extractor is lower near the bed entrance than the bed exit. The extractor is therefore disconnected and the contents mixed so that the average oil concentration in the seeds is once again the same at any point in the bed. This new average concentration is given by

$$x = x_o - (M_e/M)$$

where M denotes the weight of oil-free seeds placed initially in the extractor. (d) Steps (a) to (c) are then repeated replacing x_o by x. A series of x,y^* values can therefore be generated which represent the desired equilibrium relationship.

It may be noted that mixing the seeds in step (c) is not essential since the same result can be obtained by leaving the seeds in contact with the oil for a long time at zero solvent flow. The oil will diffuse from the rich region near the extractor outlet to the lean region near the inlet. However, since the diffusion is slow, it is preferable to mix the seeds for more rapid attainment of equilibrium.

Determination of Mass Transfer Coefficients

Equations 2 and 3 can be solved numerically provided the equilibrium relationship between the solvent and seeds is known and the parameters U, $_s$, ρ, ϵ and A_p can be determined independently. The only variable which is unknown is the mass transfer coefficient K and must be assumed for the numerical solution. The correct value of K is then found by matching the predicted and measured solvent concentration in the extractor outlet as a function of time.

Based on general leaching experience, the mass transfer coefficient depends on the solvent flow rate, the state of the seeds, the operating temperature and pressure. If the seeds are crushed or otherwise pretreated, it may be difficult to measure the interfacial area A_p. In this case, it is customary to determine the product A_pK, which is usually called the "volumetric mass transfer coefficient".

Solution of the Extraction Equations

Equations 2 and 3 which govern the oil extraction can be solved by standard numerical techniques. Of particular interest are the oil content in the effluent CO_2 and the oil profile in the seed bed as a function of time. This information is required for the design, scale-up and operation of oil extractors.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The basic instrument used in this work was a Hewlett-Packard liquid chromatograph (Model 1081B) which had been modified to permit operation with liquid carbon dioxide in the pump and supercritical carbon dioxide in the extractor. The chromatograph oven, which normally houses an HPLC column, was fitted with a small extraction vessel (10 mL) and restricter valve. The solvent chamber was converted to a flame ionization detector (FID) oven with appropriate valving and electronics. The operation of the system (schematically shown in Fig. 2) was as follows. Liquid CO_2 from storage tank (a) passed through a Nupro 5 μm filter (b), a dry ice/acetone bath (c) and then entered the cooled

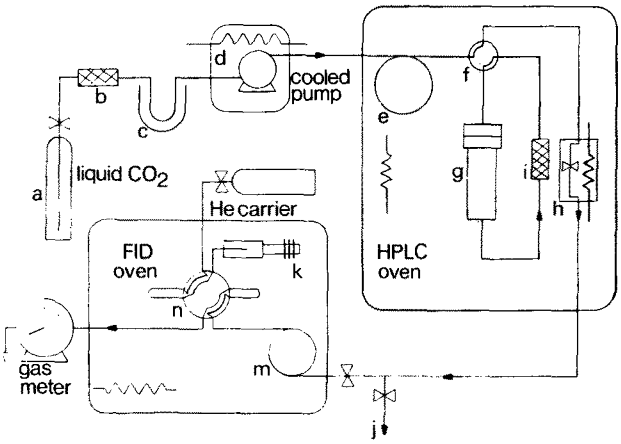

FIG. 2. Schematic diagram of supercritical fluid extraction system.

pump head (d). The cooled liquid CO_2 then flowed through pressure and flow-metering devices into the HPLC oven. In the oven, the CO_2 temperature was raised to the desired value (typically 40 C) by passing it through a 10 m long × 0.8 mm i.d. stainless steel tube (e). The supercritical fluid then flowed through a Valco 4 port, high pressure valve (f). Depending on the position of this valve, the system operated in an extraction or nonextraction mode. In the nonextraction mode, the fluid was channeled directly to a heated Nupro micro-metering valve (h). This valve was used to control the flow and pressure in the system. In the extraction mode the fluid flowed from the 4 port valve through the extraction vessel (g) and 5 μm filter (i) back into the 4 port valve and then into the flow restricter valve. The oil-bearing CO_2 leaving the extractor was collected at (j) or channeled to the flame ionization detector (k-n) for analysis. Although the FID worked well for low-boiling substances, the canola oil, due to its low volatility, tended to produce very wide peaks with tailing over a long period of time.

Procedure for Semi-Continuous Extraction

The ground seeds (4 g canola: variety Candle) to be extracted were placed in the extraction vessel, and the vessel was placed in the oven and allowed to reach the preset temperature. The vessel was isolated from the system via the 4 port valve and the pressure and flow rates of the supercritical fluid set and allowed to reach steady state. The extractor was then switched into the system and samples of the CO_2/oil mixture collected at (j) for analysis at 15 min intervals. At the termination of a run, the seeds were removed and weighed. Hexane extractions on the untreated seed and on the extracted seeds were carried out in a Goldfisch extractor.

RESULTS AND DISCUSSION

Based on the hexane extraction of crushed canola seeds, the seeds contain 40% wt of hexane extractable material. This compares favorably with the literature values for canola which range from 36-43% wt.

The quantity of oil extracted with supercritical CO_2 at 35 M Pa and 40 C from 4 g of crushed seed is shown in Figure 3. The first 15-20 min are required for the pressure and flow rate to stabilize at the desired conditions. After that time, there is a period during which the rate of oil extraction is constant, followed by a rapid decrease in the rate. The oil concentration of the supercritical CO_2 during the first linear phase was: 7.2 mg of oil/g CO_2 at a CO_2 flow rate of 1.84 g/min and 8.7 mg of oil/g CO_2 at a CO_2 flow rate of 0.64 g/min.

At 30 M Pa, 40 C and a CO_2 flow rate of 0.45 g/min this concentration dropped to 5.4 mg oil/g CO_2 and remained relatively constant for ca. 5 hr (Fig. 4).

For the design of a continuous countercurrent extractor, the relationship between the concentration of the oil in the solvent (y^*) and the seeds having an oil concentration of x is needed.

For our experimental conditions, the concentration of the oil in the solvent leaving the extractor remained constant for an extended period of time (Fig. 5). This indicates that equilibrium conditions prevailed at the outlet of the extractor and that the concentration of oil in the seeds (x) at the outlet during that time was equivalent to the initial oil concentration x_0. The concentration of oil in solvent would be equal to y^*. By repeating the experiments with crushed seed having different initial oil concentrations, the relationship between y^* and x can be established.

The effect of seed pretreatment on the equilibrium

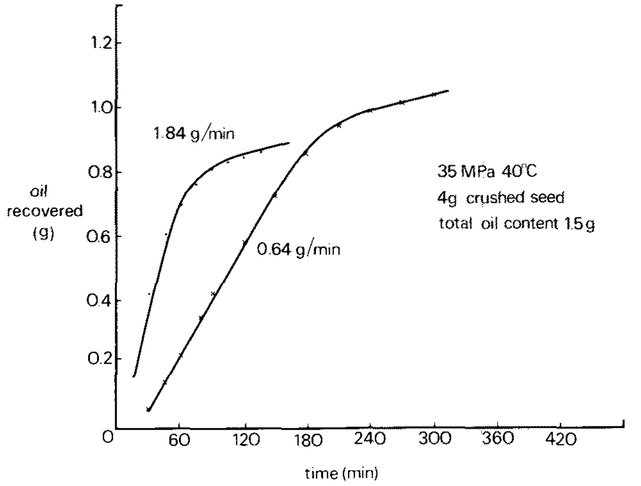

FIG. 3. Yield of canola oil recovered from 4 g of crushed seed extracted with supercritical carbon dioxide at 35 MPa and 40 C for CO_2 flow rates of 1.84 g/min and 0.64/min.

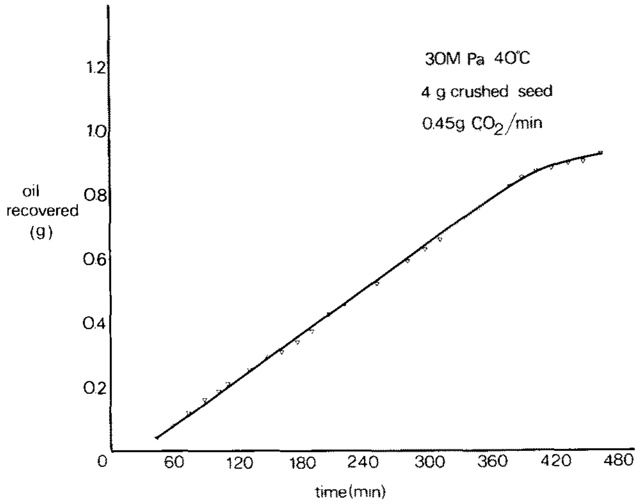

FIG. 4. Yield of canola oil recovered from 4 g of crushed seed extracted with supercritical carbon dioxide at 30 MPa and 40 C for a CO_2 flow rate of 0.45 g/min.

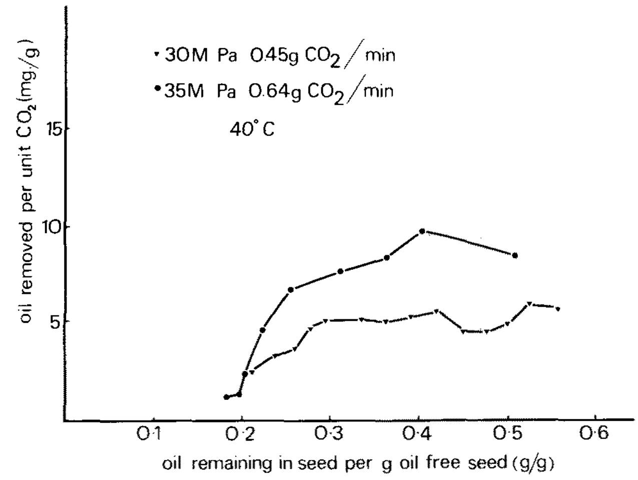

FIG. 5. Oil recovered per unit mass of CO_2 passing through the crushed canola seed for seed having different levels of oil content. Oil content of the seed is the average for the whole seed bed and is calculated as the total hexane extractable oil remaining in the seeds divided by the total g of oil-free seed.

conditions and the rate of oil removal are also under investigation. Similarly, the agreement between experimental data and theoretical predictions (based on the solution of equations 2 and 3) is still being examined.

ACKNOWLEDGMENTS

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