AN ABSTRACT OF THE THESIS OF

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Title : The Extraction of Pentachlorophenol from Pressure Treated Wood Using Supercritical Carbon Dioxide

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The extraction of pentachlorophenol (PCP) from pressure treated wood wafers with supercritical carbon dioxide has been studied. Experimental data were obtained for the effects of pressure (17.5 - 25.0 MPa), temperature (313 - 353 K), flow rate (1 - 3 ml/min at supercritical conditions), and sample size (0.8 x 10 x 50 mm and 2.2 x 10 x 50 mm) by measuring the effluent concentration versus time. A fundamental model was developed which includes rates of intraparticle diffusion, external film mass transfer, desorption and the initial distribution of PCP between the pore volume (cell lumen) and pore surface (cell wall) of wood wafers. The intraparticle diffusion and external mass transfer rates are combined in terms of an overall mass transfer coefficient derived from the assumption of a parabolic concentration profile of PCP inside the wafer pores. The initial distribution of PCP between cell lumen and cell wall was determined by fitting

the mathematical model to dynamic extraction rate data. The desorption rate was very small for all the extraction conditions, and extraction rate increased with the pressure, temperature, and flow rate because the combined mass transfer increased. Similar values of mass transfer coefficient were achieved for two different sample sizes: 0.8 x 10 x 50 mm and 2.2 x 10 x 50 mm.

The Extraction of Pentachlorophenol from Pressure Treated Wood Using Supercritical Carbon Dioxide

By

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NOMENCLATURE

Bi = Biot number = $k_f(\delta/2)/D_e$

c = PCP mass concentration in CO_2 in the extractor, g/cm^3 of bulk fluid

C = Dimensionless PCP concentration in CO_2 in the extractor = c/c_{T0}

c_i = PCP mass concentration in the pore volume of wafer, g/cm^3 of pore volume

C_i = Dimensionless average PCP concentration in the pore volume of wafer = $\langle c_i \rangle / c_{T0}$

$\langle c_i \rangle$ = Average PCP mass concentration in the pore volume of wafer, g/cm^3 of pore volume

c_{i0} = Initial PCP mass concentration in the pore volume of wafer, g/cm^3 of pore volume

c_{T0} = Initial PCP mass concentration in the wafer, g/cm^3 of wafer volume

c_s = Adsorbed PCP mass concentration in the wafer, g/cm^{3}of wafer volume

$\langle c_s \rangle$ = Volume average PCP mass concentration in the wafer, g/cm^{3}of wafer volume

c_{s0} = Initial adsorbed PCP concentration of wood wafer, g/cm^{3}of wafer volume

C_s = Dimensionless adsorbed PCP concentration in the wafer = c_s/c_{T0}

D_e = Effective interparticle diffusion coefficient for PCP in wood, cm^2/sec

E = Volume ratio in equation (28) = (volume of wafer/volume of bulk fluid) in the extractor = $N(LW\delta)/V_b$

G = Specific gravity of wood

K = Equilibrium adsorption coefficient

k_f = External mass transfer coefficient, cm/sec

k_p = Combined mass transfer coefficient = $3(k_f/(\delta/2))/(3+Bi))$, 1/sec

L = Length of wood wafer = length of extractor, 5 cm

m = Initial distribution ratio of PCP in the pore fluid total PCP in the wafer

M = Moisture content of wood, %

N = Number of wood wafer

Nu = Nusselt number = $k_f L/D_e$

R = Radius of extractor, 0.794 cm

Re = Reynolds number = $vL/\nu R^2\pi$

Sc = Schmidt number = ν/D_e

t = Time, sec

v = Volumetric flow rate of solvent, cm^3/sec

V_b = Volume of bulk fluid in the extractor = $\pi R^2 L - N\delta WL$, cm^3

W = Width of wood wafer, 1 cm

Greek Letters

α = Parameter defined in Equation (33)

β = Parameter defined in Equation (32)

δ = Thickness of the wood wafer, cm

ε = Porosity of wafer = (volume of pore/volume of wafer)

θ = Dimensionless time = t/τ

ν = Kinematic viscosity, cm^2/sec

τ = Residence time (bulk fluid volume of extractor/volumetric flow rate), sec

ϕ = Dimensionless mass transfer coefficient = $k_p\tau$

THE EXTRACTION OF PENTACHLOROPHENOL FROM PRESSURE TREATED WOOD USING SUPERCRITICAL CARBON DIOXIDE

CHAPTER 1

INTRODUCTION

1.1 PCP in Wood as a Hazardous Waste

Pentachlorophenol (PCP) was introduced as a preservative for timber and lumber in the 1930's (Hunt et al., 1967). Presently, PCP is still used extensively for the same propose. The total world-wide production of PCP was estimated to be about 30,000 metric tons annually in 1987 (International Programma on Chemical Safety, 1987). Although the usage of PCP has declined in recent years, the 1988 consumption in wood treatment plants was estimated at 9,800 metric tons (Micklewright, 1990).

While preservative treatment significantly prolongs the life of wood for utility poles, piling railroad ties and other products, these materials increasingly become the subject of concern at the end of their life cycles. These products contain chemical biocides which, although safe in the wood, pose a perceived risk as they are placed in landfills. The Environmental Protection Agency (EPA)

currently regulates disposal of treated wood based on a standard test, Toxicity Characteristic Leaching Procedure (TCLP), in which materials for disposal are subject to a leaching procedure (The Office of Federal Register, 1992). Based on this test, detection of chemicals above a certain limit classifies the material as a hazardous waste and it cannot be disposed at a regular landfill site. The current EPA regulations specify a TCLP limit of 100 ppm for PCP; however, proposed changes to these regulations would lower this level to 0.1 ppm (Old Wood, 1992). Most PCP treated wood has a TCLP of 7 to 10 ppm, and thus the majority of disposed materials would not pass the new TCLP requirements.

Currently, there are over 187 million utility poles in the United States and approximately 40 % of these poles are treated with PCP. A typical utility replaces approximately 1 to 2 % of its wooden poles each year, creating the potential for the disposal of nearly 1.5 million PCP treated poles every year. In addition, PCP has been used to treat wood for fence posts, lumber, timber, and a variety of other products. Since there is currently no commercial, effective method for safe disposal of these materials, they would have to be shipped to hazardous waste facilities. The cost of such disposal is quite high and is increasing dramatically. At the same time the large volume of disposed materials accelerates the rate at which a site reach its capacity. An industry group, Utilities Solid Waste Activities Group in Washington D.C., estimated that utility companies will spend $37.4 billion on the management of PCP treated wood as a hazardous waste if the regulatory level of preservative is changed as

planned. This projected expense would create a massive demand for effective methods for reducing the risk associated with the disposal of PCP treated wood.

1.2 Potential Remediation Technologies

Two techniques that have received attention for the removal of PCP from treated materials are bioremediation and incineration. In bioremediation the contaminated wood is chipped and placed into an environment that is conducive to fungi or bacteria that can degrade the PCP (Telephone Poles, 1991). This process results in decomposition of PCP over a period ranging from several days to several weeks and usually involves some type of soil preparation, which can be labor intensive. Studies on solid-phase and slurry-phase bioremediation of materials contaminated with PCP revealed that these bio-processes are slow and inefficient, with a maximum PCP degradation of about 50 % (Mueller et al., 1991a; Mueller et al., 1991b). Incineration, although highly effective, has been largely hampered by an inability to obtain the necessary license to burn PCP treated wood because of concerns about potential toxic fume leaks.

A third possible remediation process is supercritical fluid extraction (SCFE) of toxic chemicals from treated wood for safe disposal or further use of wood and recycling treatment chemicals. Supercritical fluids (SCFs) have been used in the removal of toxins from soils and groundwater and they are particularly useful in

reducing the volume of toxic material to be handled. The smaller volume may then be destroyed at a much lower cost.

Supercritical fluid extraction is a rapidly developing technology that has great potential for separating and purifying high value products or the removal of bound (non-extractable) pesticides from soils and plants (Deroos et al., 1990; Groves, 1985; Khan, 1988; Roop et al., 1989; Yocklovich et al., 1988). Recent studies on the removal of DDT (Khan et al., 1988; Groves, 1985), polyclorinated biphenyls (PCBs), and dioxins (Eckert et al., 1986), showed that SCFs can remove pesticides from soil matrices as well as from groundwater. In a study done on the extraction of PCP from soil, SC-CO_2 has been found to recover 240% more PCP than other solvent extraction methods like Soxhlet (Myer et al., 1992). Some researchers (Defilippi et al., 1980; Madras et al., 1993) studied the use of SC-CO_2 to regenerate activated carbon loaded with pesticides. They pointed out that the supercritical regeneration method was economical even through the operating pressure and temperature are above 150 atm and 387 °C, respectively (Defilippi et al., 1980). The application of SCFE of PCP from wood has recently been the subject of a U.S. patent application (Levien et al., 1993).

1.3 Supercritical Fluid Extraction

A supercritical fluid is a fluid that is heated above and compressed beyond its critical temperature and pressure. Supercritical fluid densities approach those

of normal liquids; however, supercritical viscosities and diffusivities are intermediate to those properties for liquids and gases. Supercritical fluids have the solvent power of liquids, but with better mass transfer capabilities. Supercritical carbon dioxide has been shown to be a potential solvent for a wide range of low vapor pressure organic chemicals. Carbon dioxide is also safe, nontoxic, relatively cheap, and readily available. When a SCF is used as a solvent, it is possible to separate a muticomponent mixture by capitalizing on both the differences in component volatilities and the differences in the specific interactions between the mixture component and the SCF solvent. Therefore the separation can have some features of distillation and some features of liquid extraction. The motivation for the development of SCF solvent technology as a viable separations technique is a result of the following:

(1) A sharp increase in the cost of energy. This has increased the cost of traditional, energy-intensive separation techniques, such as distillation.

(2) Increased governmental scrutiny and regulation of common industrial solvents, such as chlorinated hydrocarbons. Because of this, nontoxic, environmentally acceptable supercritical fluid solvents such as CO_2 are very attractive as alternative industrial solvents.

(3) More stringent pollution-control legislation. Industry must consider alternative techniques for waste treatment.

(4) Increased performance demands on materials for better separation. The traditional processing techniques cannot meet the perfect separation.

SCFE can be used to either remove variable solutes from a solid matrix or to remove undesirable chemicals and produce a solute-free solid product.

1.4 Pressure Treatment of Wood

Pressure treatment of wood with preservatives is by far the most effective method of protecting wood against attack by decay, insects, fire, and other wood-destroying agents. Over the years, numerous treating processes have been used for pressure treating wood. The rueping process (Henry, 1973), characterized as an empty-cell process, is probably the most widely used process for treatment of poles, land piles, posts, crocessties, and lumber with oilborne preservatives, such as PCP. The P-9 heavy oils are primarily used for pole, cross arm, and heavy timber treatment to improve for PCP solubility (Henry, 1973). In this process, wood is placed in the treating cylinder and air pressure is first applied to the system, filling the wood cells with compressed air. The preservative solution is then forced into the treating cylinder while the air pressure inside the cylinder is maintained constant by bleeding off air as the preservative solution enters the cylinder. When the treating cylinder is filled with preservative solution, additional pressure is applied to the system, forcing preservative into the wood and further compressing any trapped air in the wood. When the desired preservative injection has been obtained, the pressure is released, the preservative solution is returned to storage, and a vacuum is applied to the system. The

compressed air in the wood expands and forces excess preservative out of wood. Depending on the preliminary air pressure applied, the final or net preservative retention amounts can be adjusted as required, while still maintaining maximum preservative penetration.

Initial required retention of PCP in the ground-contact zone is 9.62 - 12.83 Kg/m^3 for effective protection (Henry, 1973). During the service life of treated wood there can be continuous depletion of PCP. The mean value of the concentration of PCP in leachate from old utility poles in one study has been found to be 1.92 Kg/m^3 of solution (Old Wood, 1992).

1.5 Objectives

The goal of this thesis was to investigate SCFE of PCP from pressure treated wood. Two major objectives were the measurement of rates of removal of PCP from pressure treated wood when using SC-CO_2 at different operating conditions, and the development and application of a simple fundamental model to the extraction rate data obtained.

CHAPTER 2

EXPERIMENTAL PROCEDURE AND ANALYSIS

The experimental set up was designed to observe the extraction process over a significant time period during which extracted samples were analyzed using a gas chromatograph. Experimental operating variables were the pressure, temperature and flow rate of CO_2 during extraction and the thickness and initial concentration of PCP in pressure treated wood samples.

2.1 Sample Preparation

Samples of wood chips were taken from Douglas fir heartwood blocks. Two chip sizes were used: 0.8 x 10 x 50 mm, and 2.2 x 10 x 50 mm. The description of sample orientation is shown in Figure 2-1. The chips were first dipped into a P-9 oil solution containing 5 weight percent PCP. P-9 oil is a mixture of aromatic, paraffinic and waxy petrochemical oils, and is a commercially used solvent for the pressure treatment of wood using PCP (Nicholas, 1973). The exact components of P-9 oil are unknown. After dipping, the chips were subjected to a vacuum (0.09 MPa) for 30 minutes in the treatment plant vessel, which has 51 cm diameter and 305 cm length. The chips were then

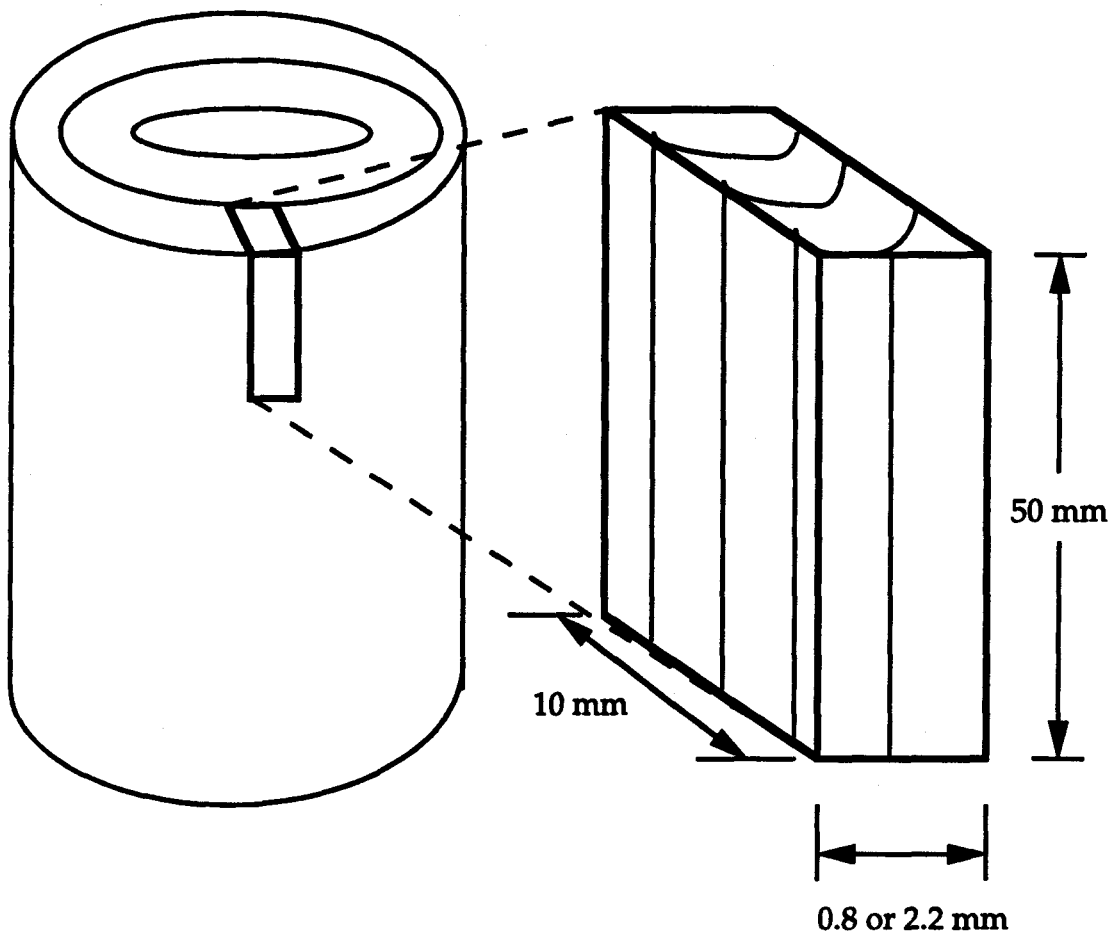


Figure 2-1. Description of sample wafer orientation.

pressure treated with P-9 oil and PCP solution for one hour at 25 °C and 125 psig. After the treatment, the surface of samples were allowed to dry for two days at room temperature (25 °C, atmospheric pressure). The porosity was determined to be 0.73, which is calculated as $\varepsilon = 1 - G(0.667+0.01\ M)$ (Siau, 1984). The specific gravity of untreated wood, G, was taken as 0.351, which was measured for untreated wood wafers. The moisture content (weight percent, weight of moisture per weight of complete dried wood) of the wood samples, M, is taken as 10, which is normal value at the wood sample storage area. The apparent density was estimated by using the average of sample weight and average of sample volume. The estimated values of the apparent densities of wood wafers are 0.71 g/cm^3 for 0.8 x 10 x 50 mm samples and 0.97 g/cm^3 for 2.2 x 10 x 50 mm samples, respectively. To determine the initial loading of PCP in the treated wood, each sample was ground to pass a 20 mesh screen using a Wiley mill, and the dust was analyzed using an x-ray florescent analyzer (Asoma 8620). Because this is a destructive method, the initial PCP concentrations of extracted chips were estimated by taking the average value of other pieces from the same treatment batch. The average initial concentrations of PCP in the wood wafers were 23.07 (±1.77) Kg/m^3 for 0.8 x 10 x 50 mm samples, and 35.86 (±1.28) Kg/m^3 for 2.2 x 10 x 50 mm samples. The accuracy of x-ray florescent analyzer was checked using known concentration of samples. The error of x-ray analyzer was maximum ± 5 % of concentration.

2.2 Equipment

The experimental apparatus used in this study was an Isco series 2000 system, which includes dual syringe pumps, extractor, and pump control system. The schematic diagram of the experimental set up is shown in Figure 2-2. Liquid carbon dioxide was allowed to flow into the cylinder of a syringe pump, which was jacket-cooled to 12 °C using a circulation chiller (VWR 1156). The wood wafers were individually separated with copper wire (0.9 mm diameter and 70 mm length) and placed in the extraction vessel (5.04 cm height and 1.59 cm diameter). The copper wire was used to prevent the wood wafers from sticking to each other. For each run, eight wafers (0.8 x 10 x 50 mm samples) or four wafers (2.2 x 10 x 50 mm samples) were loaded in the extraction vessel. The compressed fluid was allowed to flow into the preheater to reach the desired extraction temperature before it entered the extractor. The temperature of the preheater and extractor were maintained at the desired value within ± 1 °C. Pressure was constantly maintained within ± 0.07 MPa by a factory-calibrated pressure transducer. The flow rate was controlled by manually adjusting a micrometring valve (Autoclave Engineering 10VRMM2812). The pump's piston displacement rate was displayed on a control board with an accuracy of ± 0.1 ml/min. The transfer tubing and micrometring valve were kept at the same temperature as the extractor by use of a heating coil (Glas-Col 103ADET0.256) to prevent precipitation of PCP.

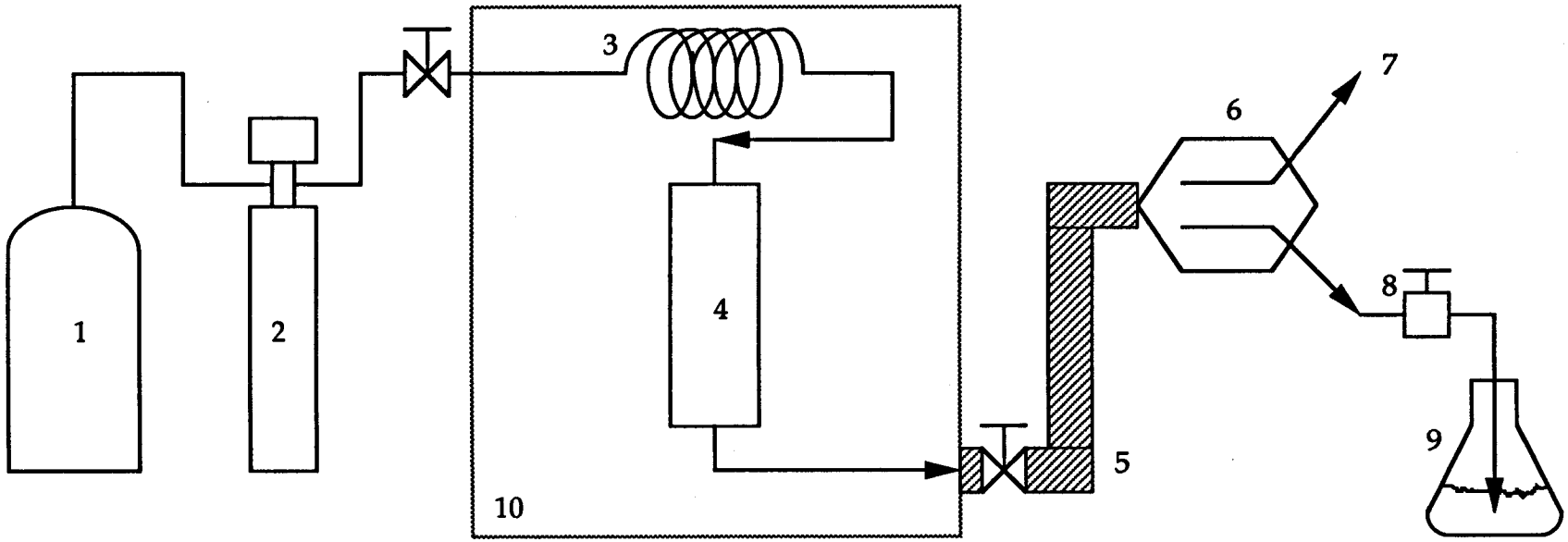


Figure 2-2. Schematic diagram of the experimental setup. 1. CO_2 tank, 2. syringe pump, 3.preheater, 4. extractor, 5. heated tubing, 6. six-port sampling valve, 7. sample port, 8. micrometring valve, 9. cold trap, 10. heated oven.

2.3 Operational Procedure

The syringe pump (ISCO 260D) was filled with liquid carbon dioxide from the feed tank. The extractor oven was turned on and allowed to reach the desired temperature. The extraction cartridge was filled with wood wafers, that were kept from touching each other by copper wire. The extractor then allowed 30 minutes to obtain thermal equilibrium, after which it was filled and pressurized to a desired pressure with CO_2. After stabilizing the pressure for 3 minutes, flow was established through at the desired flow rate by adjusting the micrometring valve. It is assumed that the extraction start from this moment. The outlet flow bubbled through an acetone cold trap to capture the PCP from the flow. During an experiment, the effluent flow was frequently sampled using the sampling valve (Valco C6U1380) and the effluent concentration of PCP was measured.

2.4 Sampling Method

A 6-port sampling valve (Valco C6U1380) was used to take 2 ml samples of the extraction product stream. Figure 2-3 shows details of the sample loop (Valco 90808). When the sample loop is switched out of the system, the fluid expands into the transfer lines between valve A and B. The total volume of the sample loop and transfer lines is approximately 5 ml. As a result of this

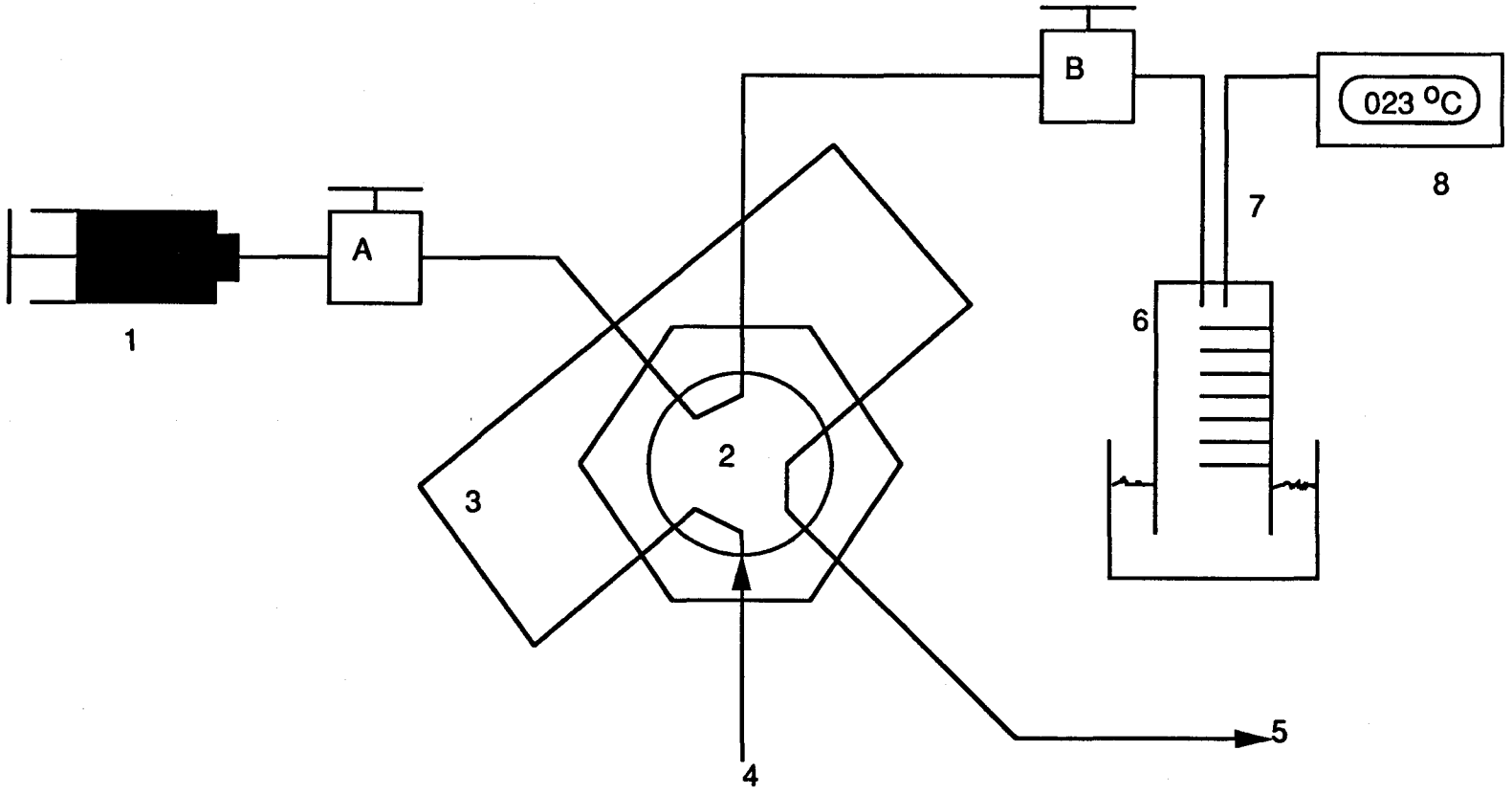


Figure 2-3. Sampling technique used to capture the samples. 1. syringe, 2. six-port sampling valve, 3. 2ml sample loop, 4. fluid from extractor, 5. fluid to micrometering valve, 6. graduated tube, 7. thermocouple, 8. temperature display.

expansion into the transfer lines, some of the PCP and oil precipitates in the lines. The amount of CO_2 in the sample loop can be ascertained by slowly opening valve B to vent the CO_2 into a graduated tube (i.e. a 1000 ml graduated tube with the bottom removed with accuracy of ± 5 ml) filled with CO_2-saturated water (PH = 4.0) at a known temperature. As the CO_2 expands to atmospheric pressure, its solvent power drops significantly and the solid solute quickly precipitates from the solution. A slow flow ensures that the PCP remains in the sample loop. The volume of CO_2 vented from the sample loop is equal to the volume of the displaced water. The PCP precipitated in the sample loop and transfer line is removed by replacing the graduated tube shown in Figure 2-3 with a volumetric flask and flushing 7 ml of acetone through the system at valve A. The amount of PCP in the acetone solution is then determined by gas-chromatography. Because of the detection limit of gas-chromatography, the flushed PCP solution should not be too dilute. Also, enough acetone should be used to devolve all of the precipitated PCP in the sample loop and the transfer line. A 7 ml flushing with acetone was found to be adequate in previous trial runs because even the more acetone was used, the captured PCP amount was not changed.

2.5 Gas-Chromatography Analysis

A Hewlett Packard 5840A gas chromatograph equipped with a flame ionization detector was used to analyze PCP in acetone solution. The column

was a 183 x 0.2 cm (i.d.) Deactiglass packed with 3 % OV-101 on 80 - 100 mesh chromosorb WHP. The oven was operated isothermally at 160°C, and the detector and injector temperatures were 250 °C and 180 °C respectively. The carrier gas flow (nitrogen) was 30 ml/min and the air and hydrogen gas head pressures were 28 psig and 15 psig, respectively.

Because PCP is a nonvolatile compound, a derivatization method with MSTFA (N-methyl-N-trimethyl-silyltrifluoracetamide) as the reagent was used as a sample injection method (U.S. EPA, 1982; MILLER, 1988; KNAPP, 1979). A 10 µl syringe (Unimetric 1-9005) was used and filled in the following order: 1 µl acetone, 1 µl air, 1 µl MSTFA, and 5 µl sample solution. The gas chromatography calibration was done using standard solutions that ranged from 25 - 200 ppm of PCP, and the ppm of PCP was determined as a function of area ratio using a linear least-square regression of the data. Every time the samples were analyzed for each run, the gas-chromatograph was calibrated for PCP before and after the analysis. Figure 2-4 shows an example of a calibration curve used to calculate the PCP concentration.

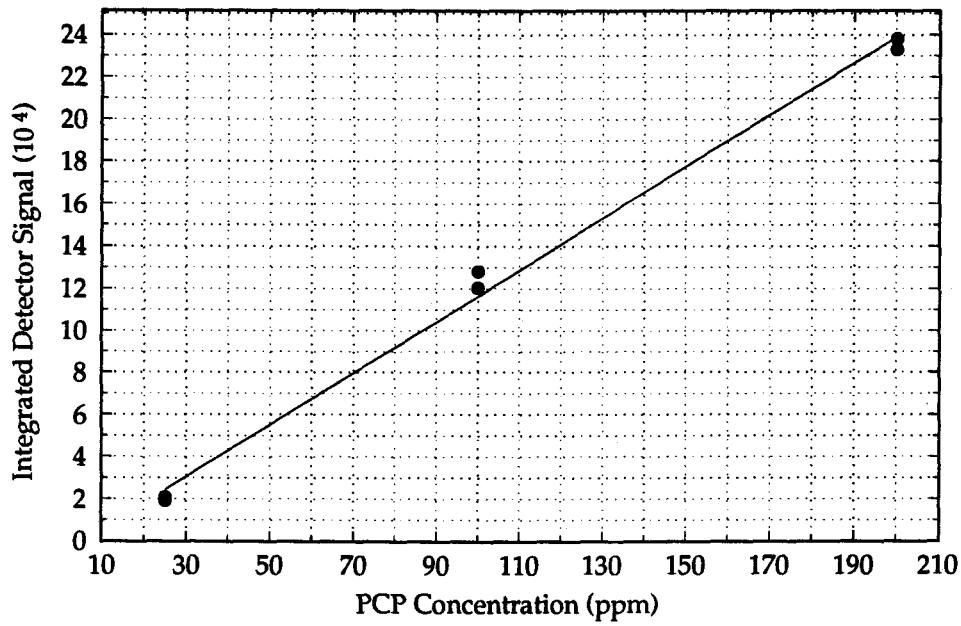


Figure 2-4. Calibration curve for GC analysis: column temperature = 160 °C, detector temperature = 250 °C, injector temperature = 180 °C.

CHAPTER 3

MATHEMATICAL MODEL

3.1 Development of Governing Equations

The extractor was filled with N wood wafers with an initial PCP loading of concentration c_{T0}. Initially the solvent rapidly fills the pore of wood wafers. Since the extractor is not large, it was approximated as a differential extractor with no axial concentration changes in the wood or fluid. The wood wafers are assumed to be initially isothermal with a uniform distribution of PCP. The porosity, permeability, and humidity of the wood are assumed to be constant. Pure solvent fluid is fed to the extractor which is operated at a constant pressure and temperature. Since the thickness of a wafer (δ) is very small compared to its width (W) and length (L), it is assumed that the dominate diffusion flux is in the x-direction over the shortest ($\delta/2$) maximum distance. Diffusion fluxes in the y and z directions are thus neglected.

With these assumptions the mass balance for the solute (PCP) in the bulk fluid phase is:

Rate of accumulation = Input rate - Output rate + Transfer rate from fluid in pores

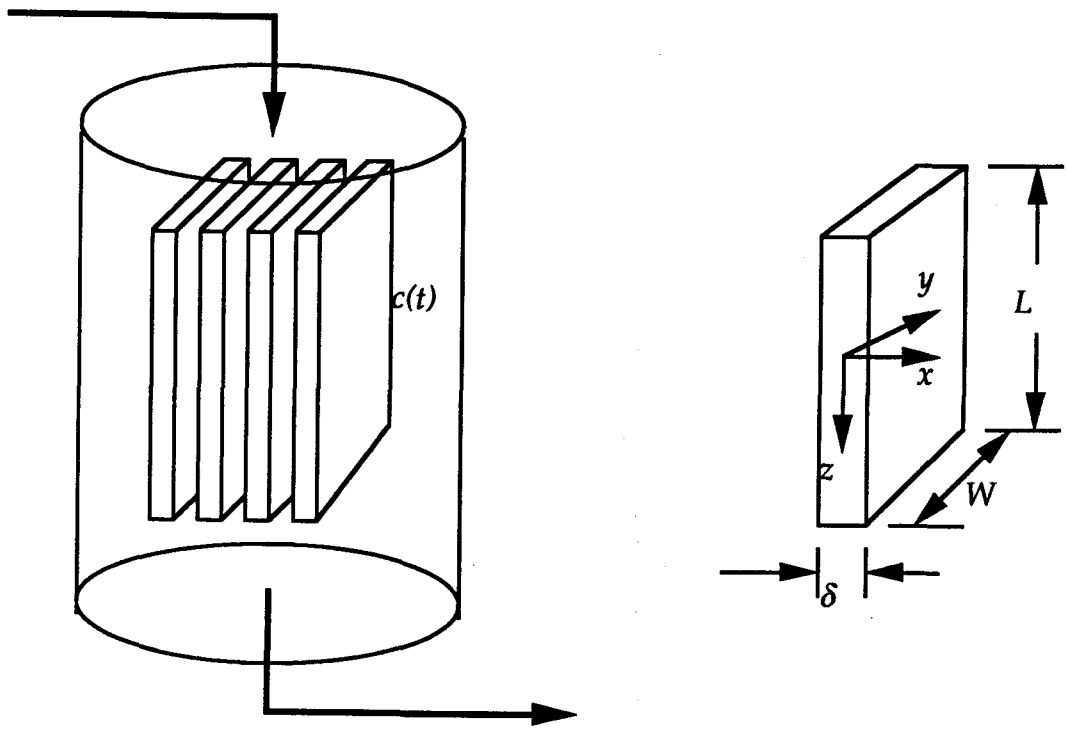


Figure 3-1. Mass balance for the solute in the bulk fluid for PCP extraction system from wood wafers.

Where

Accumulation = Rate of accumulation of mass of PCP in the bulk fluid

$= d\{(\pi R^2 L - N\delta LW)c\}/dt = L(\pi R^2 - N\delta W)dc/dt = V_b dc/ct$

Input rate = Bulk flow of PCP into the extractor = 0

Output rate = Bulk flow of PCP out of extractor = vc

Transfer rate = Transfer of PCP from fluid in pores wood wafer to bulk fluid = $Nk_f(c_i|_{x=\delta/2} - c)2WL$

Therefore, the mass balance for the solute in the bulk fluid (c) can be written as:

$$\frac{dc}{dt} = -\frac{c}{\tau} + \frac{N(2LW)}{V_b}k_f(c_i|_{\frac{\delta}{2}} - c) \qquad (1)$$

where $\tau = V_b/v$.

The mass balance for PCP in the fluid in pores of a differential wafer volume with Δx thickness is:

Rate of accumulation = Input rate - Output rate + Transfer rate from wood to pore volume fluid

where

Accumulation = Rate of mass of PCP accumulated in the fluid in the pores of wafer = $\partial(\Delta x WL\varepsilon c_i)/\partial t = \Delta x WL\varepsilon(\partial c_i/\partial t)$

Input rate = Effective diffusion of PCP into the differential volume element of wafer = $-(D_e\partial c_i/\partial x)WL|_{x=x}$

Output rate = Effective diffusion of PCP out of differential volume element of wafer = $-(D_e\partial c_i/\partial x)WL|_{x=x+\Delta x}$

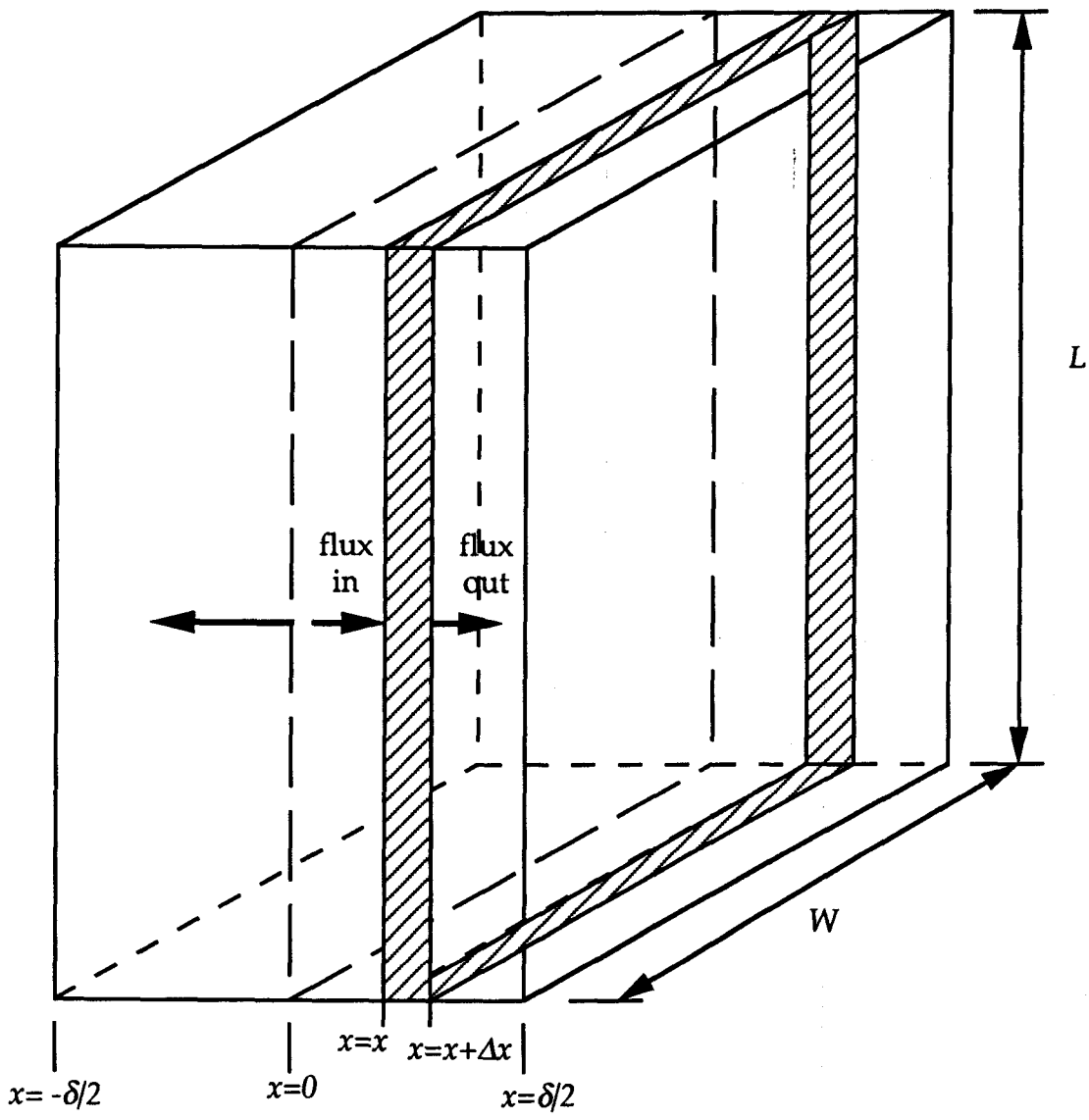


Figure 3-2. Differential volume element within the wood wafer.

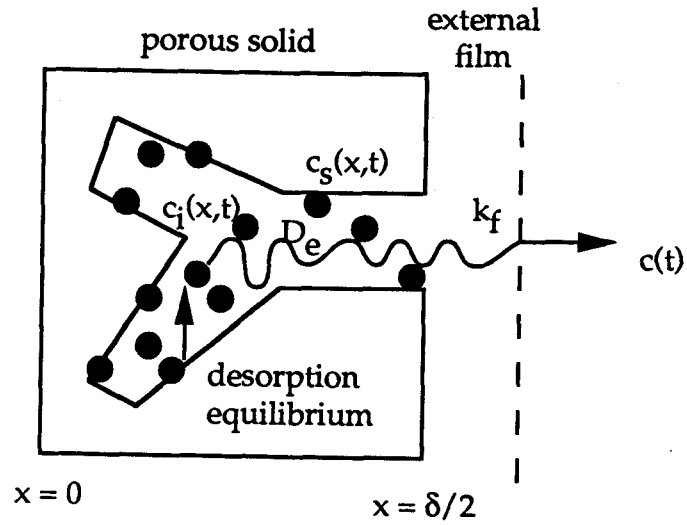


Figure 3-3. Schematic diagram of inside of wood wafer.

Transfer rate = Transferred of PCP from wood to pore volume fluid

$= - \Delta x WL(\partial c_s/\partial t)$

Dividing by the differential volume ($\Delta x WL$) and in the limit as $\Delta x \rightarrow 0$, the differential mass balance for the solute in the pore volume can be written as:

$$\varepsilon \frac{\partial c_i}{\partial t} = D_e \frac{\partial^2 c_i}{\partial x^2} - \frac{\partial c_s}{\partial t} \qquad (2)$$

On the surface of pores inside the wafer (cell wall), it is assumed that the adsorbed PCP concentration and concentration in the pore fluid are in equilibrium with a linear adsorption isotherm, so that:

$$\frac{\partial c_s}{\partial t} = K \frac{\partial c_i}{\partial t} \qquad (3)$$

3.2 Conditions

Because PCP has only a weak chemical affiliation to the cell walls, some PCP is initially in the pore volume fluid within the wafer (cell lumen) without any interaction to the cell wall. The total amount of PCP is therefore assumed to be distributed between two different locations: in the pore volume of the wafer (cell lumen) or at the surface of wood cells (cell wall). Initially, the total concentration in mass of PCP per total wafer volume is:

$$c_{T0} = \varepsilon c_{i0} + c_{s0} \tag{4}$$

Next a the partition coefficient of initial distribution of PCP in the pore fluid of the wood wafers to the total amount of PCP (m) is defined as:

$$m = \frac{\varepsilon c_{i0}}{c_{T0}} = 1 - \frac{c_{s0}}{c_{T0}} \tag{5}$$

Physically m is the fraction of total initial PCP that is in the pore volume fluid, and is thus bounded by 0 and 1. For $m \approx 0$, essentially all of PCP in the wood is on the surface of the wood cell wall. For $m \approx 1$, all of PCP is in the pore volume fluid (cell lumen) of the wafer.

The boundary and initial conditions then become:

$$\frac{\partial c_i}{\partial x} = 0 \qquad at\ x = 0 \quad for\ t > 0 \tag{6}$$

$$-D_e \frac{\partial c_i}{\partial x} = k_f(c_i - c) \qquad at\ x = \frac{\delta}{2} \quad for\ t > 0 \tag{7}$$

$$c = 0 \qquad at\ \ t = 0 \tag{8}$$

$$c_i = c_{i0} = \frac{m}{\varepsilon} c_{T0} \qquad at\ t = 0 \quad for\ -\frac{\delta}{2} \le x \le \frac{\delta}{2} \tag{9}$$

$$c_s = c_{s0} = (1 - m)c_{T0} \qquad at\ t = 0 \quad for\ -\frac{\delta}{2} \le x \le \frac{\delta}{2} \tag{10}$$

Figure 3-4 shows the geometrical locations of boundary conditions.

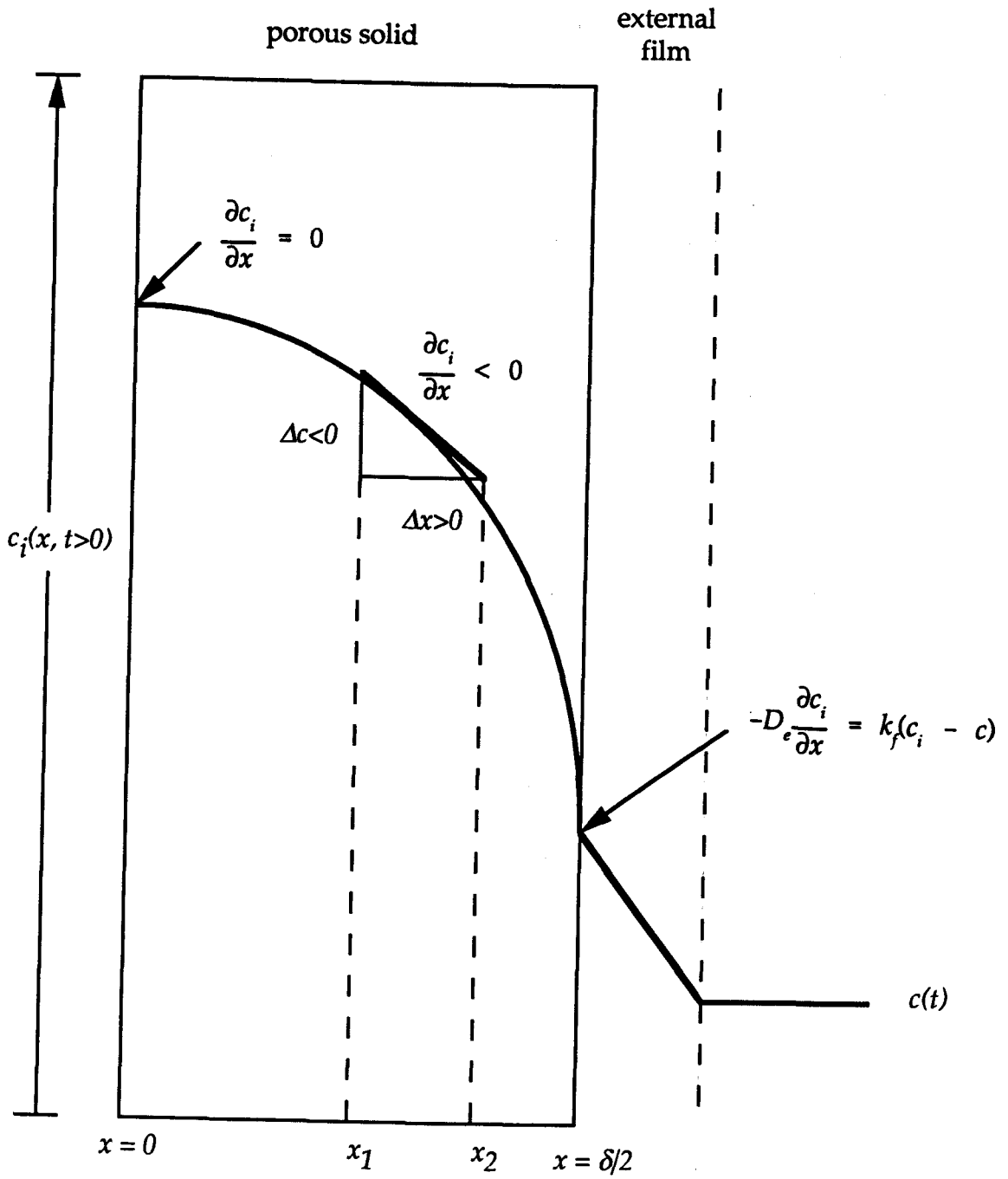


Figure 3-4. Boundary conditions of the concentration of PCP in the pore of wood wafer.

3.3 Parabolic Profile Approximation

Because of the inclusion of intraparticle diffusion in Equation(2) with boundary conditions (6) and (7), significant numerical effort is required to solve these differential equations. However, several studies have simplified the equations by assuming that the intraparticle concentration profile has a parabolic shape at all times (Liaw et al., 1979; Rice, 1982; Tomida et al., 1987). Such a simplification is intuitive, however, researchers have found that the approximate solutions obtained by using the parabolic profile are remarkably simple and agree well with the exact solution except for a brief initial period (Do et al., 1986; Goto et al., 1990a; Rice et al., 1983). This assumption has also been used in the studies of ethyl acetate extraction from activated carbon using supercritical carbon dioxide (Srinivasan et al., 1990) and supercritical fluid extraction of caffeine from coffee beans (Pecker et al., 1992).

A parabolic concentration profile for PCP in the pore volume fluid can be written:

$$c_i(x,t) = a(t) + b(t)x^2 \qquad (11)$$

This can be substituted into Equation (2) and boundary conditions, Equations (6) and (7).

Substituting Equation (11) into Equation (7) and evaluating at $x = \delta/2$:

$$c = a(t) + \left((\frac{\delta}{2})^2 + \frac{2D_e(\frac{\delta}{2})}{k_f} \right) b(t) \qquad (12)$$

The average concentration of PCP in the pore fluid, $<c_i>$ can be defined and Equation (11) used to find:

$$<c_i> = \frac{1}{(\frac{\delta}{2})WL} \int_0^{\frac{\delta}{2}} WLc_i dx = a(t) + \frac{1}{3}(\frac{\delta}{2})^2 b(t) \qquad (13)$$

By the substituting Equation (13) from Equation (12), $b(t)$ can be expressed as a function of c and $<c_i>$:

$$b(t) = \frac{c - <c_i>}{\frac{2}{3}(\frac{\delta}{2})^2 + \frac{2D_e(\frac{\delta}{2})}{k_f}} \qquad (14)$$

Integrating both sides of Equation (2) from $x = 0$ to $x = \delta/2$ and dividing by half the wafer thickness, we obtain:

$$\varepsilon \frac{\partial}{\partial t} \left(\frac{\int_0^{\frac{\delta}{2}} c_i dx}{(\frac{\delta}{2})} \right) = \frac{D_e \int_0^{\frac{\delta}{2}} \frac{\partial^2 c_i}{\partial x^2} dx}{(\frac{\delta}{2})} - \frac{\partial}{\partial t} \left(\frac{\int_0^{\frac{\delta}{2}} c_s dx}{(\frac{\delta}{2})} \right) \qquad (15)$$

The left hand side of Equation (15) must be the same as $\varepsilon(d<c_i>/dt)$ from Equation (13). The second term of right side of Equation (15) written in terms

of the volume average concentration of c_s, which is defined as:

$$<c_s> = \frac{1}{WL(\frac{\delta}{2})}\int_o^{\frac{\delta}{2}} WLc_s dx \tag{16}$$

Doing so Equation (15) can be written as:

$$\varepsilon\frac{d<c_i>}{dt} = \frac{D_e}{(\frac{\delta}{2})}\int_0^{\frac{\delta}{2}}\frac{\partial^2 c_i}{\partial t^2}dx - \frac{d<c_s>}{dt} \tag{17}$$

Substituting c_i from Equation (11) into the right hand side of Equation (17) yields:

$$\varepsilon\frac{d<c_i>}{dt} = 2D_e b(t) - \frac{d<c_s>}{dt} \tag{18}$$

Substituting b(t) from Equation (14) yields:

$$2D_e b(t) = k_p(c - <c_i>) \tag{19}$$

where k_p is an overall average mass transfer coefficient defined as:

$$k_p = \frac{3k_f/(\frac{\delta}{2})}{3 + Bi} \tag{20}$$

and Bi is the Biot number which is:

$$Bi = \frac{k_f(\frac{\delta}{2})}{D_e} \tag{21}$$

Substituting Equation (19) into Equation (18) then yields the final form of equation for the time derivative of $<c_i>$:

$$\varepsilon\frac{d<c_i>}{dt} = k_p(c - <c_i>) - \frac{d<c_s>}{dt} \tag{22}$$

Starting with Equation (1), Equation (11) can be used to evaluate $c_i\,|_{x=\delta/2}$ and Equation (12) substituted for c to yield:

$$\frac{dc}{dt} = -\frac{c}{\tau} + \frac{N(2LW)}{V_b}\left(-2b_e(\frac{\delta}{2})b\right) \tag{23}$$

Substitution for $2D_eb$ from Equation (19) yields the final equation for the derivative of c:

$$\frac{dc}{dt} = -\frac{c}{\tau} - \frac{N(2LW)(\frac{\delta}{2})}{V_b}k_p(c - <c_i>) \tag{24}$$

Using the definitions of $<c_i>$ and $<c_s>$, Equation (3) can be used to obtain an equation relating the time derivatives of these two average as:

$$\frac{d<c_s>}{dt} = K\frac{d<c_i>}{dt} \tag{25}$$

3.4 Analytical Solution

Equation (25) can be used to eliminate $\langle c_s \rangle$ from Equation (22) and Equations (22) and (24) can then be rewritten in dimensionless variables: $C = c/c_{T0}$, $C_i = \langle c_i \rangle / c_{T0}$, $\theta = t/\tau$, and $\phi = k_p \tau$.

$$\frac{dC_i}{d\theta} = \left(\frac{\phi}{\varepsilon + K}\right)(C - C_i) \tag{26}$$

$$\frac{dC}{d\theta} = -C - E\phi(C - C_i) \tag{27}$$

where

$$E = \frac{N(WL\delta)}{V_b} \tag{28}$$

Where the initial conditions then become:

$$C = 0 \quad at \quad \theta = 0 \tag{29}$$

$$C_i = \frac{m}{\varepsilon} \quad at \quad \theta = 0 \tag{30}$$

Equations (26) - (30) can be solved using the Laplace transform to yield $C(\theta)$ and $C_i(\theta)$. Since $C(t)$ data can be obtained as discussed previously, the solution for $C(\theta)$ is important for parameter estimation and has the form:

$$C(\theta) = \frac{mE\phi}{2\varepsilon\alpha}\left(\exp\left(\frac{(-\beta+\alpha)}{2}\theta\right) - \exp\left(\frac{(-\beta-\alpha)}{2}\theta\right)\right) \tag{31}$$

Where

$$\beta = 1+(\frac{1}{\varepsilon+K}+E)\phi > 0 \quad (32)$$

$$\alpha = (\beta^2-\frac{4\phi}{\varepsilon+K})^{\frac{1}{2}}, \quad thus\ 0 < \alpha < \beta \quad (33)$$

Equation (31) shows that the effluent concentration responds as a second order dynamic system and three unknown parameters: a desorption rate coefficient (K), a combined mass transfer coefficient (k_p), and the initial distribution ratio (m). The combined mass transfer coefficient depends on the external mass transfer coefficient (k_f) and effective intraparticle diffusion coefficient (D_e) and arises because of the parabolic concentration profile approximation for c_i as a function of x. Therefore, it is possible to determine the combined mass transfer coefficient, desorption rate constant, and initial distribution ratio from experimental data of bulk PCP concentration (c) as a function of time.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Experimental Results

The supercritical fluid extraction(SFE) of PCP from wood wafers using CO_2 was performed to study the effects of pressure, temperature, flow rate, and sample thickness. For studying the effect of pressure, extraction experiments were conducted at 17.5, 20.0, 22.5, and 25.0 MPa at a fixed temperature of 353 K and a feed flow rate of 2 ml/min. To study the influence of temperature, three different temperatures of 313, 333, and 353 K, were used and pressure and flow rate were held constant at 22.5 MPa and 2 ml/min, respectively. For the flow rate effect, three flow rates of 1, 2, and 3 ml/min, were selected at the conditions of 22.5 MPa, 353 K. All these extractions were conducted on 0.8 x 10 x 50 mm samples with an initial PCP concentration of 23.07 (±1.77) Kg/m^3 of wafer. As an initial check for thickness effects, additional data were obtained on wafers with a thickness of 2.2 mm at 22.5 MPa, 353 K, and 2 ml/min of flow rate. The initial concentration of these thicker samples, however, was 35.86 (±1.28) Kg/m^3 of wafer, or 55% higher than with the thinner wafers. Thus the effects of wafer thickness and initial loading have not been independently investigated.

Table 4-1. Experimental Conditions.

Pressure (MPa)	Temperature (K)	Flow* Rate (cm^3/min)	Sample** Thickness (mm)	PCP Extracted (g)	% Extracted	PCP Collected (g)
(1) Pressure Variance						
17.5	353	2	0.8	0.0319	43.0	0.0175
20.0				0.0439	57.5	0.0223
22.5				0.0514	70.9	0.0267
25.0				0.0549	72.9	0.0249
(b) Temperature Variance						
22.5	313	2	0.8	0.0496	63.5	0.0212
	333			0.0465	60.0	0.0213
	353			0.0514	70.9	0.0267
(c) Flow Rate Variance						
22.5	353	1	0.8	0.0469	60.7	0.0191
		2		0.0514	70.9	0.0267
		3		0.0491	63.4	0.0235
(d) Sample Thickness Variance						
22.5	353	2	0.8	0.0514	70.9	0.0267
			2.2	0.0882	63.7	Not avail.

* Flow rate is at supercritical conditions (T, P).
** Sample size is thickness x 10 x 50 mm.

All these extractions are performed for 60 minutes. The summary of operating conditions and the total amount of PCP removed are listed in Table 4-1. The fifth and sixth columns in Table 4-1 show the amount of PCP extracted and extracted percentage for each set of conditions. Those values are calculated by taking the difference between an average initial concentration of wafers from the same treatment batch and the final concentration of extracted wood wafers obtained using an X-ray florescent analyzer. The last column shows the amount of PCP collected in the acetone cold trap during extraction and cleaning the tubing, measured with a gas chromatograph. But the amount does not include the amount of PCP removed during the depressurizing after the extraction runs. Therefore the differences between PCP extracted and PCP collected are estimated as the removed amounts during the venting procedure.

Figures 4-1 to 4-4 show time dependent concentrations of PCP in the effluent stream for different extraction conditions. During the extractions P-9 oil is also extracted and some of PCP can be extracted with oil components. These results include the amounts of PCP extracted with oil. Experimental results show that for most cases, the effluent concentration of PCP increased rapidly during the first few minutes of extraction and then decreased gradually. Most of the extraction occurred within the first 20 minutes. Madras et al. (1993) found similar behavior when studying supercritical fluid regeneration of activated carbon by removal of heavy molecular weight organics, such as naphthalene, phenanthrene, hexachlorobenzene and PCP.

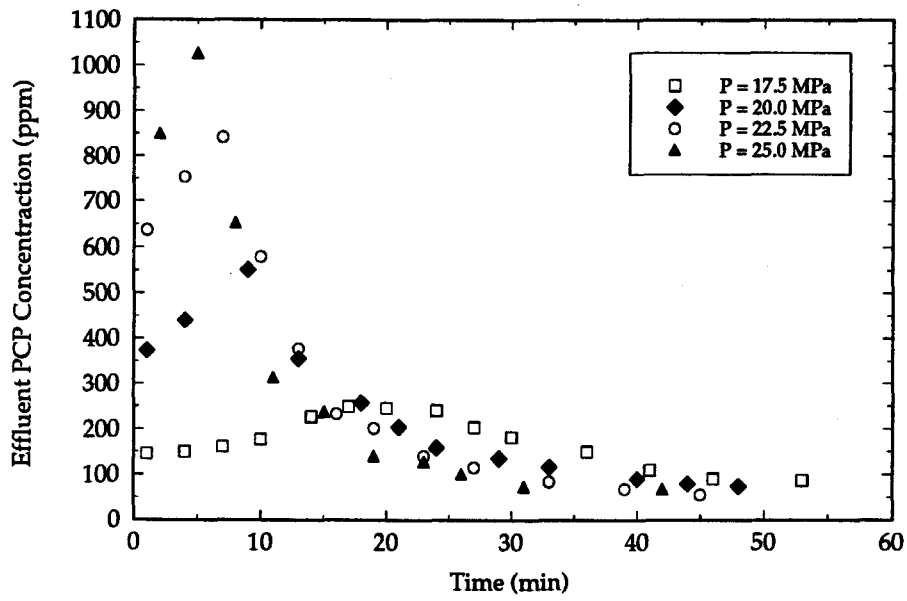


Figure 4-1. Effect of pressure on PCP concentration in extract at 353 K and 2 cm^3/min for 0.8 x 10 x 50 mm samples.

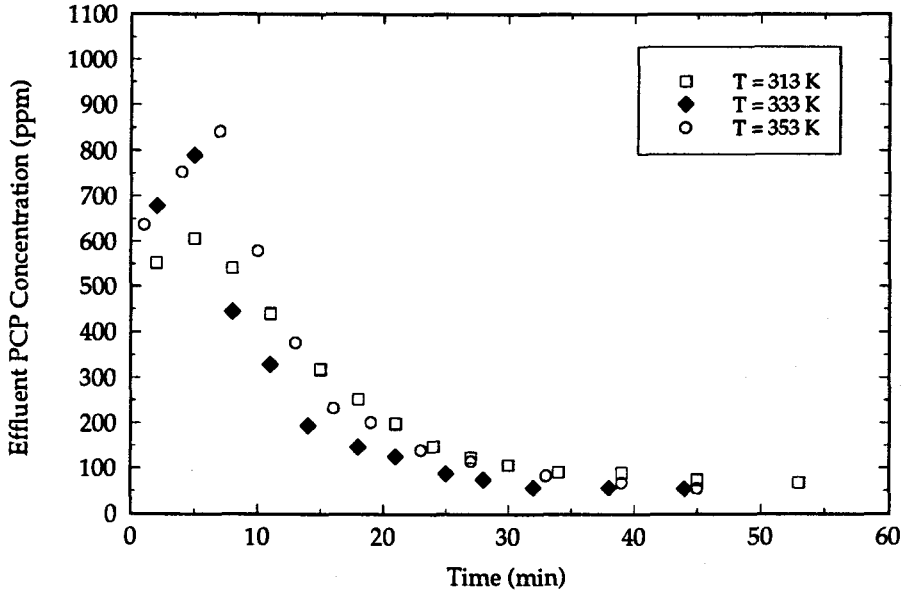
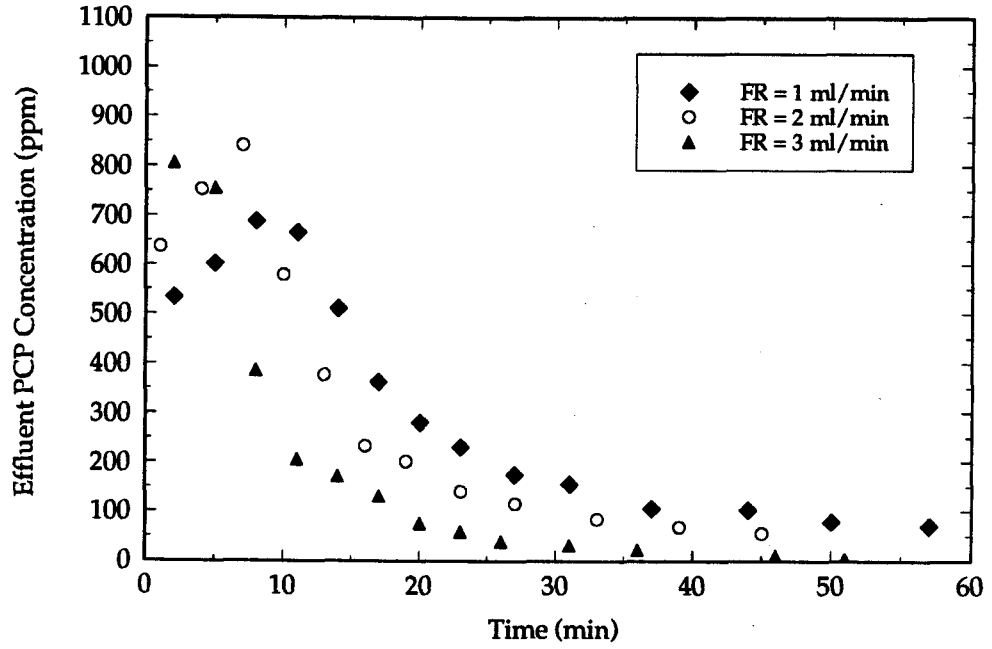
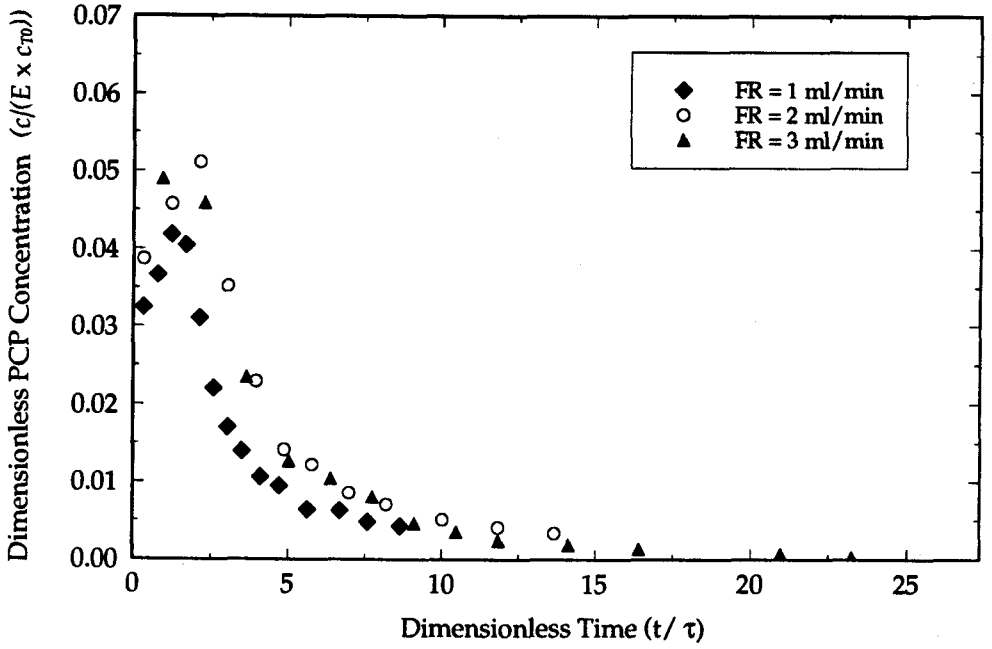
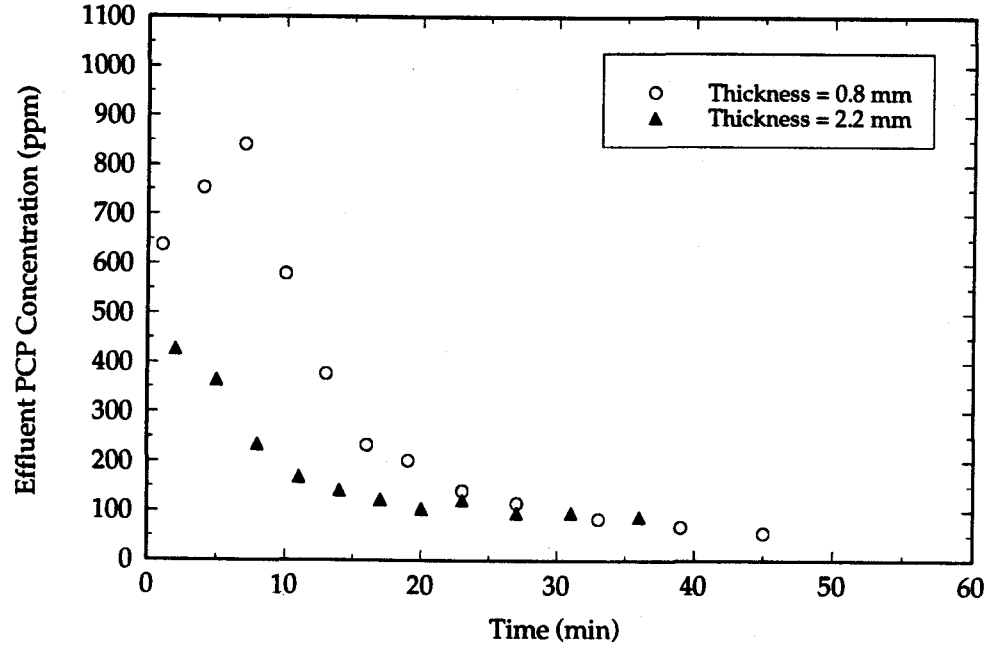


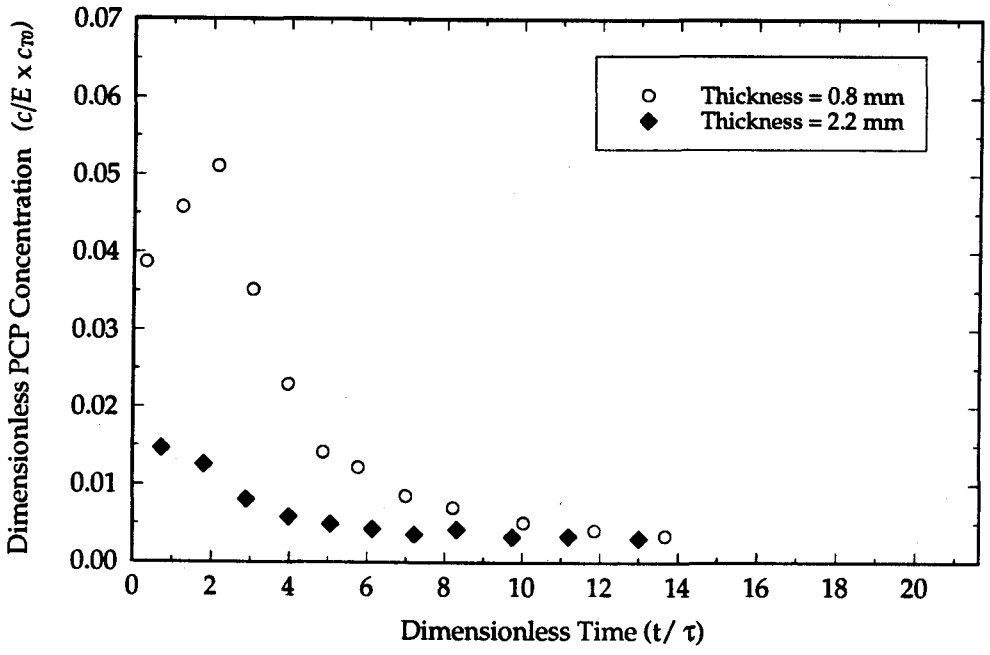
Figure 4-2. Effect of temperature on PCP concentration in extract at 22.5 MPa and 2 cm^3/min for 0.8 x 10 x 50 mm samples.





Figures 4-3a, 4-3b. Effect of flow rate on PCP concentration in extract at 22.5 MPa and 353 K for 0.8 x 10 x 50 mm samples (a) with dimension (b) without dimension.





Figures 4-4a, 4-4b. Effect of sample thickness on PCP concentration in extract at 22.5 MPa, 353 K and 2 cm^3/min (a) with dimension (b) without dimension.

Curves of similar shape have been observed for caffeine extraction from coffee beans (Peker et al., 1992), lignin extraction from wood (Goto et al., 1990b), and ethyl acetate extraction from activated carbon (Srinivasan et al.,1990).

At higher pressures, the extraction rate increased (Figure 4-1). Increased temperature and flow rate also were observed to increase the initial rate of extraction (Figures 4-2 and 4-3). Figures 4-3b and 4-4b show dimensionless PCP concentration histories versus a dimensionless time scale. The x-axes of those graphs are actual time divided by the space time of SC-CO_2 in the extraction vessel. The y-axes of Figures 4-3b and 4-4b are the ratio of effluent PCP concentration divided by the initial PCP concentration in the wood wafers and volume ratio of wafers and extractor. The integrated area of the graph from time zero to infinite should be one for complete extraction. This expression explains the efficiency of extraction using unit mass of solvent. In Figure 4-3b, there is improvement of extraction when flow is increased from 1 to 2 ml/min. However, for an additional increase from 2 to 3 ml/min, there is little effect on extraction rate. Thus 2 ml/min appears to be an upper bound or an effective flow rate. Figure 4-4 indicates that the rate of extraction decreased for a thicker sample, even though the initial loading was higher.

The reproducibility of the experiments was checked at four different conditions. Figures 4-5 to 4-8 show one pair of repeated runs each. These show reasonable reproducibility except at the highest pressure, 25 MPa, in Figure 4-6. Because the initial PCP concentration used is an average, the inaccuracy of initial

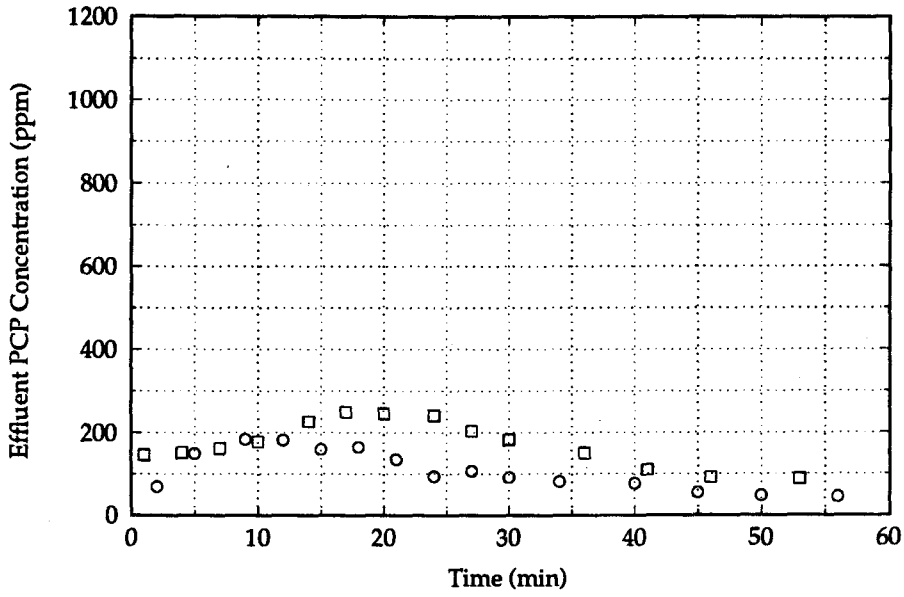


Figure 4-5. Repeated runs at 17.5 MPa, 353 K and 2 cm^3/min for 0.8 x 10 x 50 mm samples.

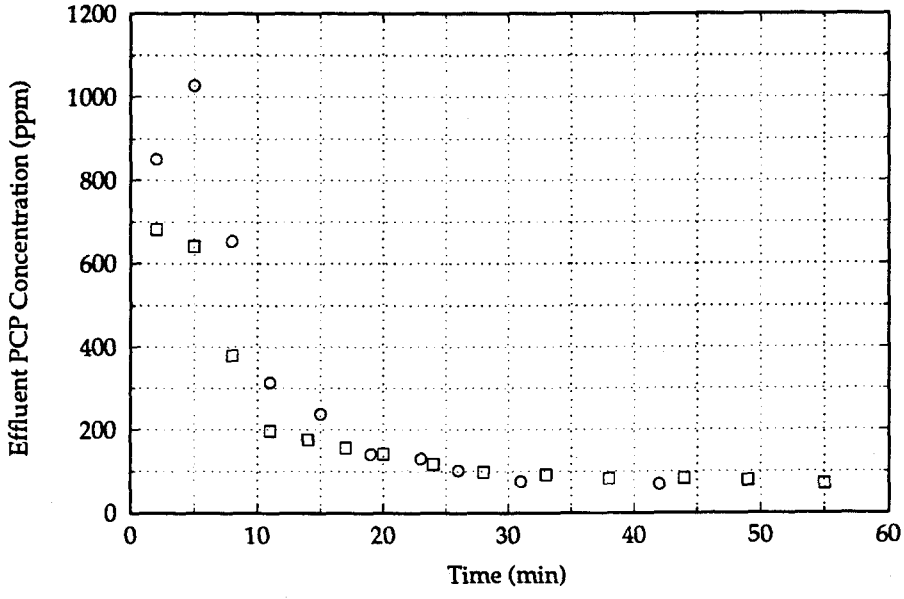


Figure 4-6. Repeated runs at 25.0 MPa, 353 K and 2 cm^3/min for 0.8 x 10 x 50 mm samples.

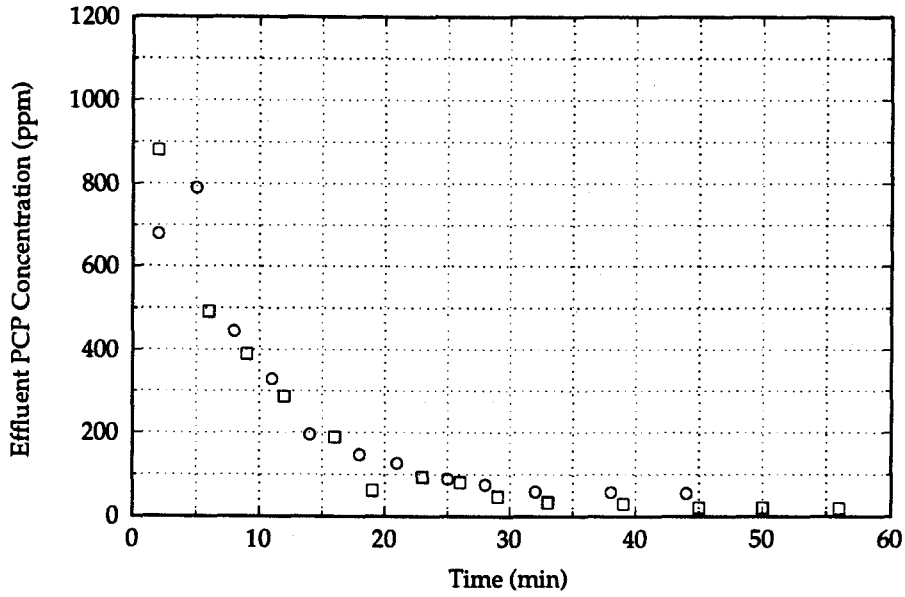


Figure 4-7. Repeated runs at 22.5 MPa, 333 K and 2 cm^3/min for 0.8 x 10 x 50 mm samples.

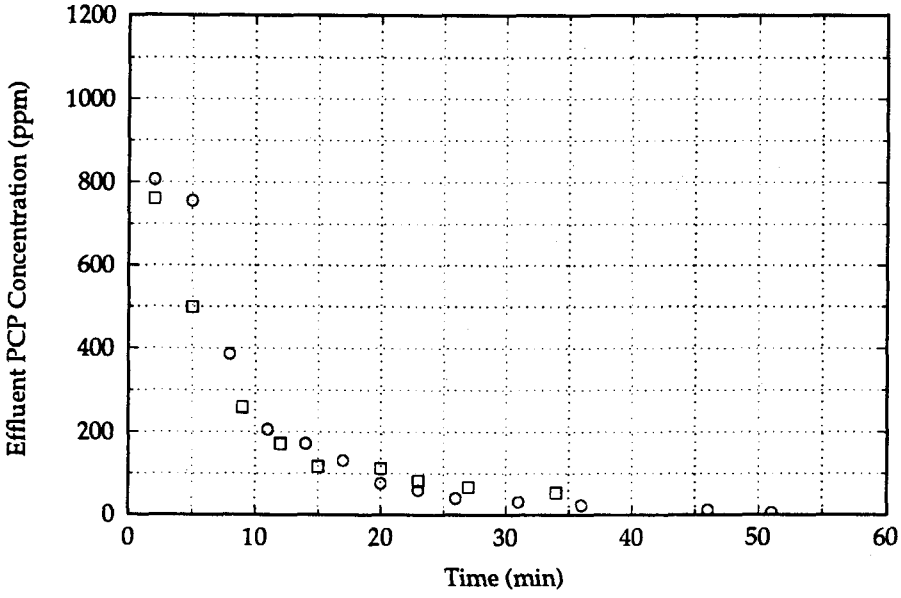


Figure 4-8. Repeated runs at 22.5 MPa, 353 K and 3 cm^3/min for 0.8 x 10 x 50 mm samples.

PCP concentration is considered as the main reason for differences between any two repeated runs.

4.2 Results of Mathematical Modeling

The effluent extraction data have been fitted in an optimal least-squares criteria by choice of parameters: K, k_p and m in Equation (31) with $\varepsilon = 0.73$. Table 4-2 contains these estimated values and the last column shows the total extracted PCP during each extraction as calculated by integrating the experimental data using Lagrange's cubic equation. Figures 4-9 to 4-12 contain model curves based on these parameters and the data for each run graphed to show the effects of operation variables. In general the model was able to fit the shape of the data for most conditions.

As shown in Table 4-2, in all cases the desorption rate coefficient (K) was very small. This means that the desorption rate of PCP from the pore surface (cell wall) of wood wafers to the pore volume (cell lumen) of wood was very small compared to the change of PCP concentration in the pore volume of the wood wafer. The values of the initial distribution ratio (m) was around 0.2 (average; 0.20 ± 0.05) for the 0.8 mm thickness samples. This means that initially, about 20 percent of the total PCP is in the pore fluid in the wood wafer without any interactions with surface of wood. For the thicker samples (2.2 mm), the estimate of the initial distribution ratio was only 0.06.

Table 4-2. Estimated Model Parameters for Various Conditions.

Press. (MPa)	Temp. (K)	Flow* Rate (cm^3/min)	K x 10^6	k_p x 10^3 (1/sec)	m x 10^2	Extracted amount (g)
Sample thickness = 0.8mm, c_{T0} = 23.07 Kg/m^3, E = 0.504						
17.5	353	2	3.38	0.21	28.7	0.0095
20.0	353	2	0.00	1.03	20.7	0.0145
22.5	313	2	4.00	1.35	20.1	0.0214
22.5	333	2	1.00	3.04	15.8	0.0162
22.5	353	1	0.80	1.80	13.2	0.0102
22.5	353	2	0.01	2.17	21.6	0.0175
22.5	353	3	0.10	3.12	21.0	0.0168
25.0	353	2	1.20	3.12	20.1	0.0198
Sample thickness = 2.2 mm, c_{T0} = 35.86 Kg/m^3, E = 0.787						
22.5	353	2	1.00	2.13	6.3	0.0097

* Flow rate is at supercritical conditions (T, P).
Sample size is thickness x 10 x 50 mm
Porosity of sample (ε) is 0.73

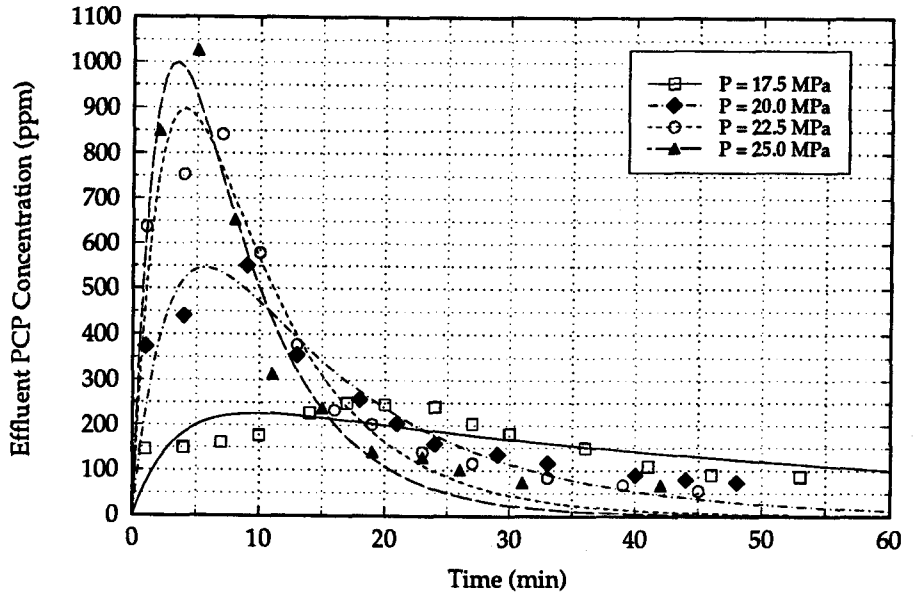


Figure 4-9. Best fit of PCP extraction histories using three model parameters for four pressures at 353 K, 2 cm^3/min and 0.8 mm wafer thickness.

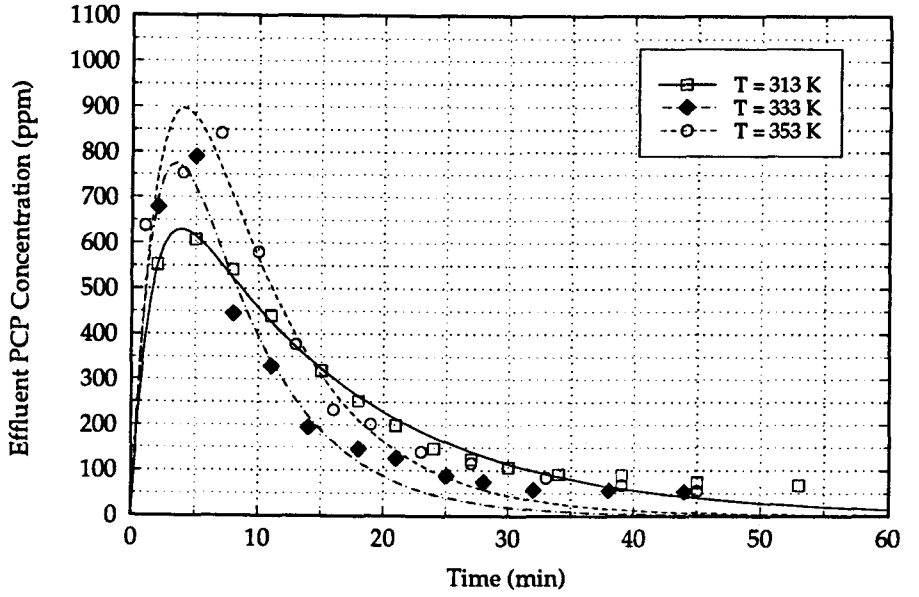


Figure 4-10. Best fit of PCP extraction histories using three model parameters for three temperatures at 22.5 MPa, 2 cm^3/min and 0.8 mm wafer thickness.

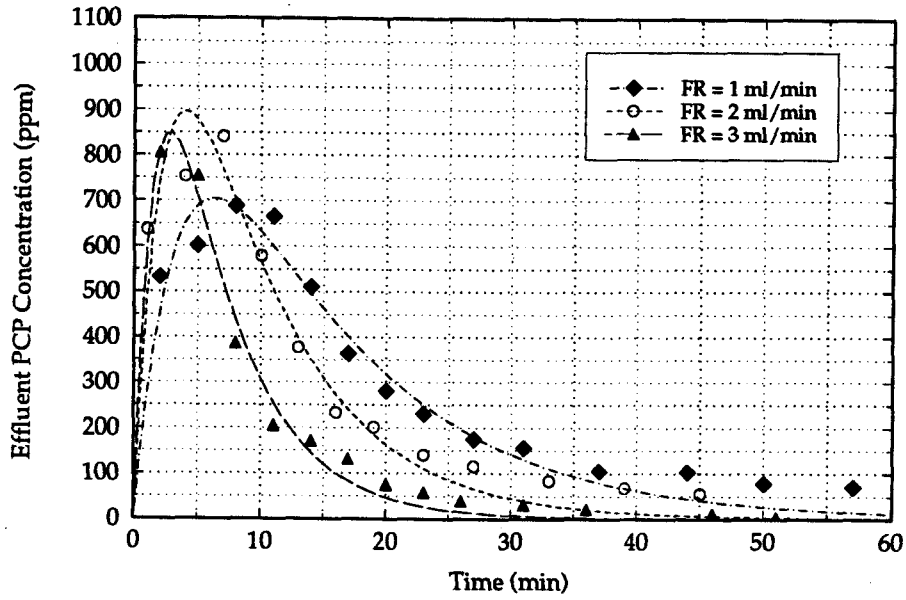


Figure 4-11. Best fit of PCP extraction histories using three model parameters for three flow rates at 22.5 MPa, 353 K and 0.8 mm wafer thickness.

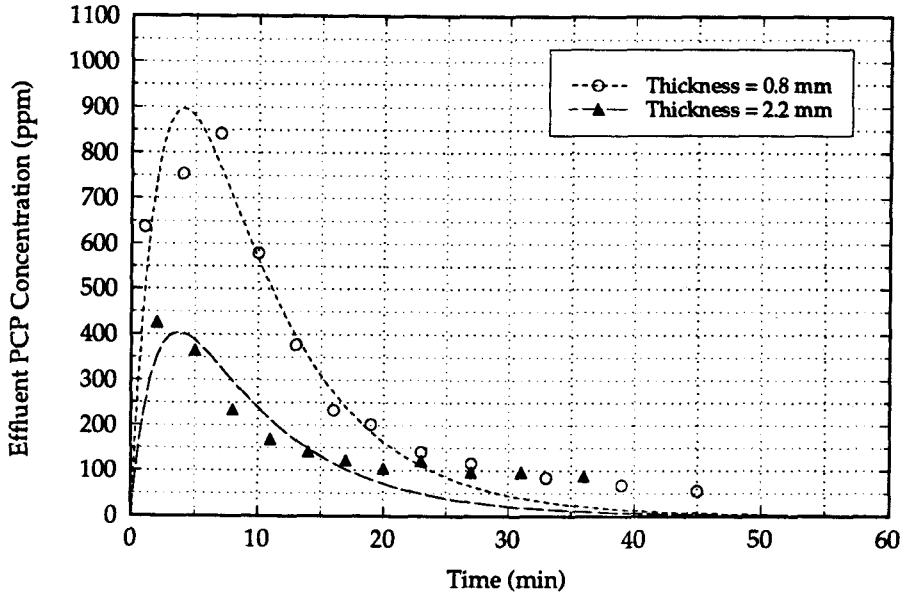


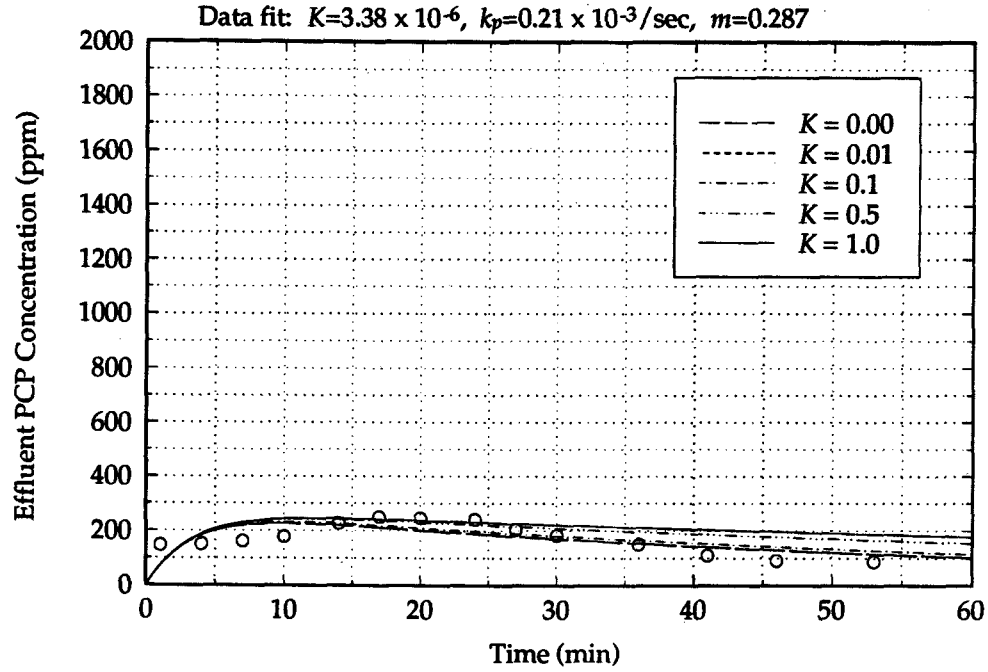
Figure 4-12. Best fit of PCP extraction histories using three model parameters for two wafer thicknesses at 22.5 MPa, 353 K and 2 cm^3/min.

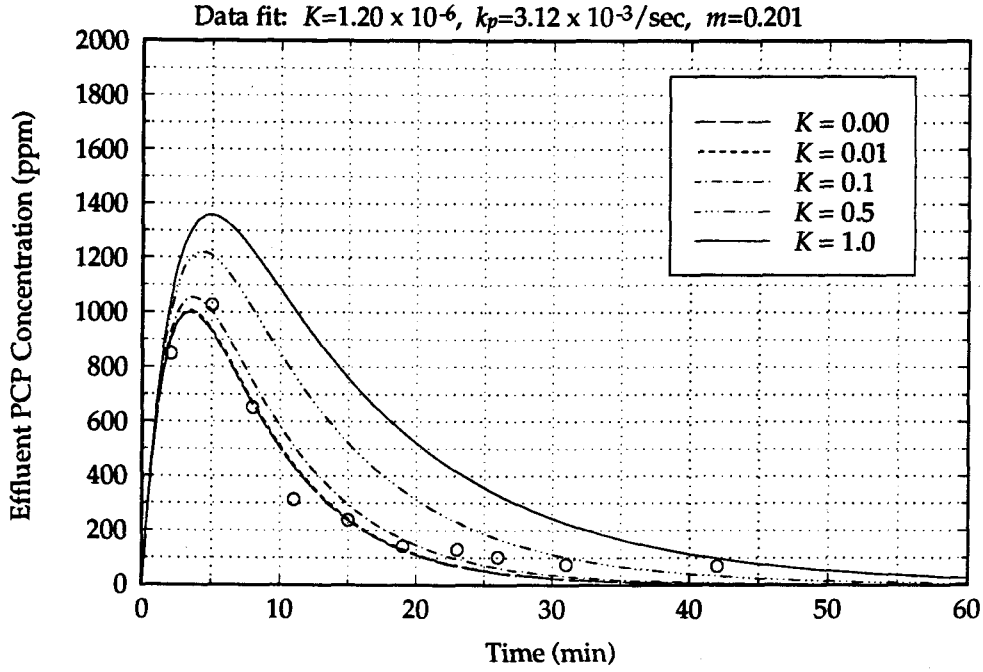
4.2.1 Three Parameter Sensitivities

The effects of each model parameter were investigated in Figures 4-13 to 4-15. In each case one parameter was varied from its base value to produce several model curves. Both low (17.5 MPa) and high (25.0 MPa) pressures were used as base cases at 353 K and 2 cm^3/min flow rate for extraction of 0.8 mm wafers. Figure 4-13 shows that the model curve is not sensitive to the value of the desorption rate coefficient (K) for values below 0.01. As K increases, the predicted effluent concentration of PCP increases at all extraction times. At higher pressure (25.0 MPa), as K increases a larger peak concentration of PCP in the effluent is predicted.

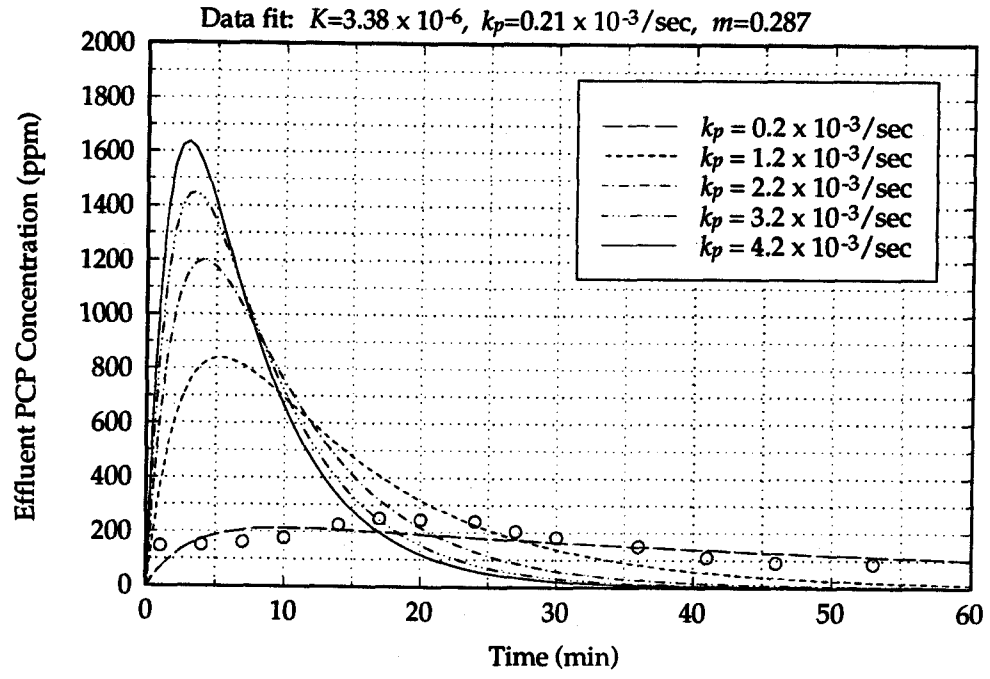
The sensitivity of the model to the combined mass transfer coefficient (k_p) is shown in Figure 4-14. At the lower pressure, higher k_p results in a faster initial removal of PCP and a much larger maximum concentration in the extract. At higher pressure, the maximum concentration increases only slightly for increased k_p.

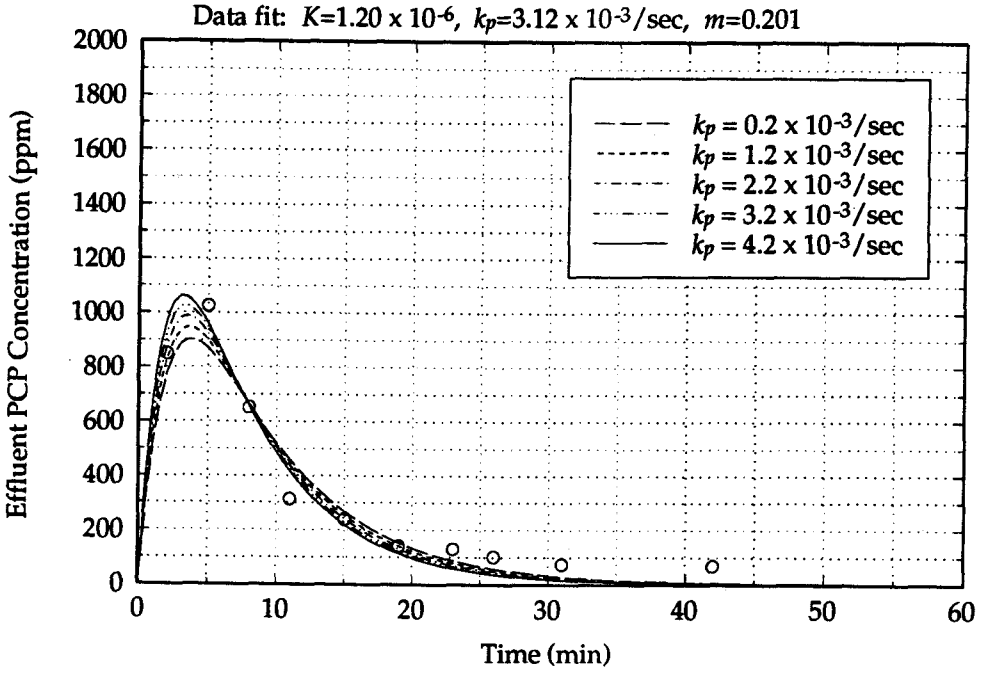
Figure 4-15 shows the model sensitivity to the initial distribution coefficient (m). At both pressures the effluent PCP concentration increased nearly uniformly at any time as m was increased. The time at which the maximum concentration occurs was nearly independent of m and occurred earlier at the higher pressure than at the lower one. This is probably due to the increased solvent strength of the SCF at higher pressures.



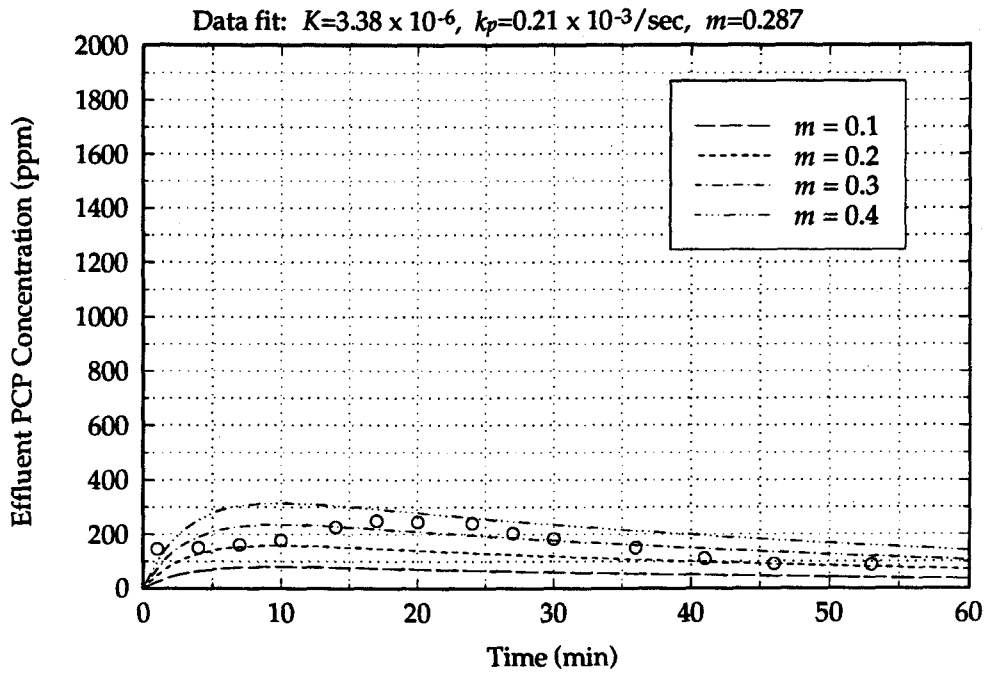


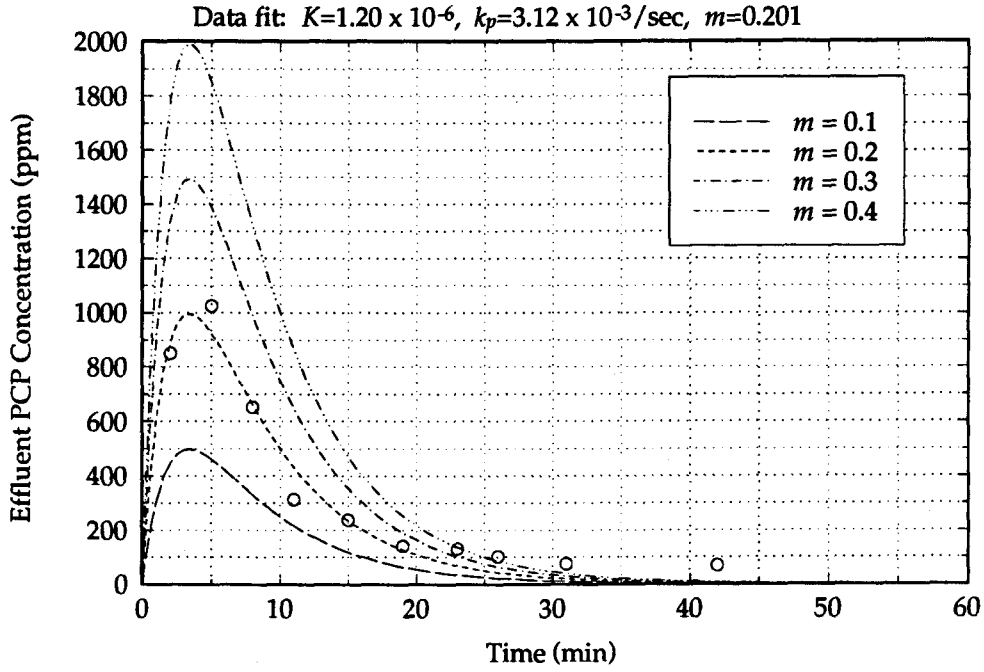
Figures 4-13a, 4-13b. Sensitivity of desorption coefficient at 353 K, 2 cm^3/min and 0.8 x 10 x 50 mm samples (a) 17.5 MPa (b) 25.0 MPa.





Figures 4-14a, 4-14b. Sensitivity of combined mass transfer coefficient at 353 K, 2 cm^3/min and 0.8 x 10 x 50 mm samples (a) 17.5 MPa (b) 25.0 MPa.





Figures 4-15a, 4-15b. Sensitivity of initial distribution ratio at 353 K, 2 cm^3/min and 0.8 x 10 x 50 mm samples (a) 17.5 MPa (b) 25.0 MPa.

4.3 One Parameter Modeling: The Combined Mass Transfer Coefficient

Based on the results shown in Table 4-2, an attempt was made to simplify the model. Because the model is not sensitive for K values below 0.01, K was taken to be zero for the cases. This implies that the PCP extracted during these experiments was present initially in pore fluid and that $c_s(x,t)$ stayed nearly constant. Since m represents an initial ratio it might be expected that it would be constant for wafers of the same size and c_{T0}. Although the fitted value of m appeared to decrease slightly with increasing temperature, most of the values were about 0.2 for wafers with 0.8 mm thickness. For the 2.2 mm wafers at higher c_{T0} the fitted m value was much smaller (0.06).

At fixed values, $K = 0$ and $m = 0.20$ or 0.06 for 0.8 mm samples and 2.2 m samples, respectively, the optimal values of the k_p were recalculated for each run based on one parameter optimization. Table 4-3 lists the experimental conditions and best values found for k_p. Figures 4-16 to 4-19 show the best one parameter curves and data for extracted PCP. The combined mass transfer coefficient, k_p, which is developed from a parabolic concentration profile of PCP in the wood wafer, simultaneously accounts for diffusion effects inside the wood wafer and external convective mass transfer effects. The expression of k_p is shown at Equation (20). For the study of caffeine extraction from coffee beans, Peker et al. (1992) reported values of the combined mass transfer coefficients between 0.004/sec and 0.022/sec at various supercritical extraction conditions. Also,

Table 4-3. Estimated Combined Mass Transfer Coefficient for Various Conditions.

Pressure (MPa)	Temperature (K)	Flow Rate* (cm^3/min)	$k_p \times 10^3$ (1/sec)
Sample thickness = 0.8 mm, c_{T0} = 23.07 Kg/m^3, E = 0.504, c_{i0} = 8942 ppm K = 0.0, m = 0.20			
17.5	353	2	0.34
20.0	353	2	1.07
22.5	313	2	1.36
22.5	333	2	2.16
22.5	353	1	0.83
22.5	353	2	2.40
22.5	353	3	3.31
25.0	353	2	3.14
Sample thickness = 2.2 mm, c_{T0} = 35.86 Kg/m^3, E = 0.787, c_{i0} = 3035 ppm K = 0.0, m = 0.06			
22.5	353	2	2.13

* Flow rate is at supercritical conditions (T. P).
Sample size is the thickness x 10 x 50 mm.
Porosity of sample (ε) is 0.73

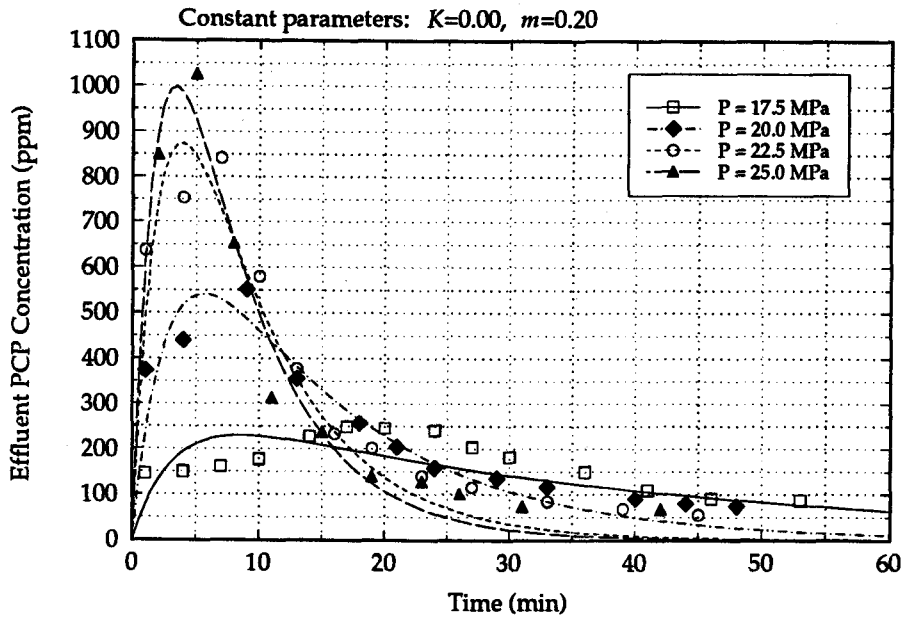


Figure 4-16. Best fit of PCP extraction histories using one model parameter for four pressures at 353 K, 2 cm^3/min and 0.8 mm wafer thickness.

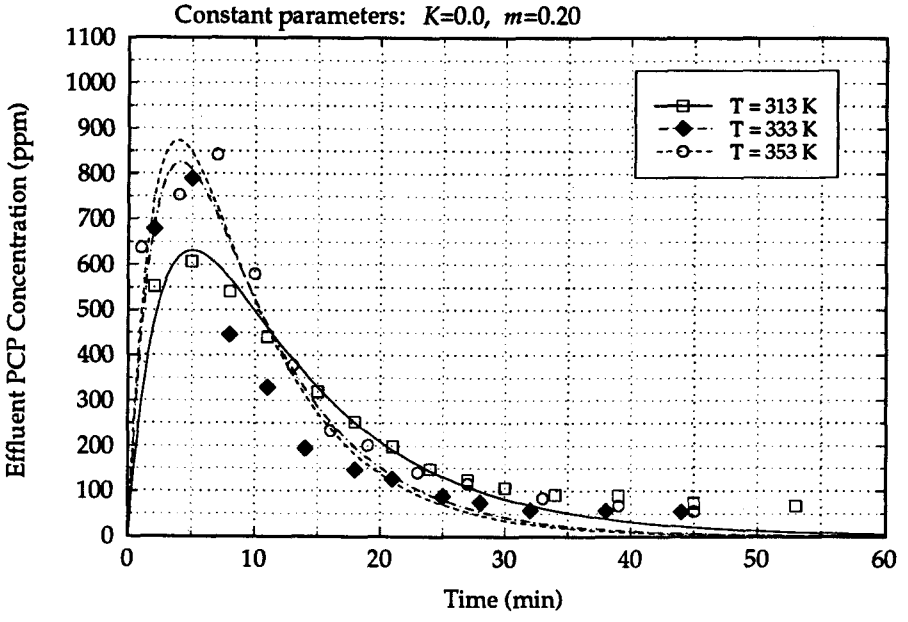
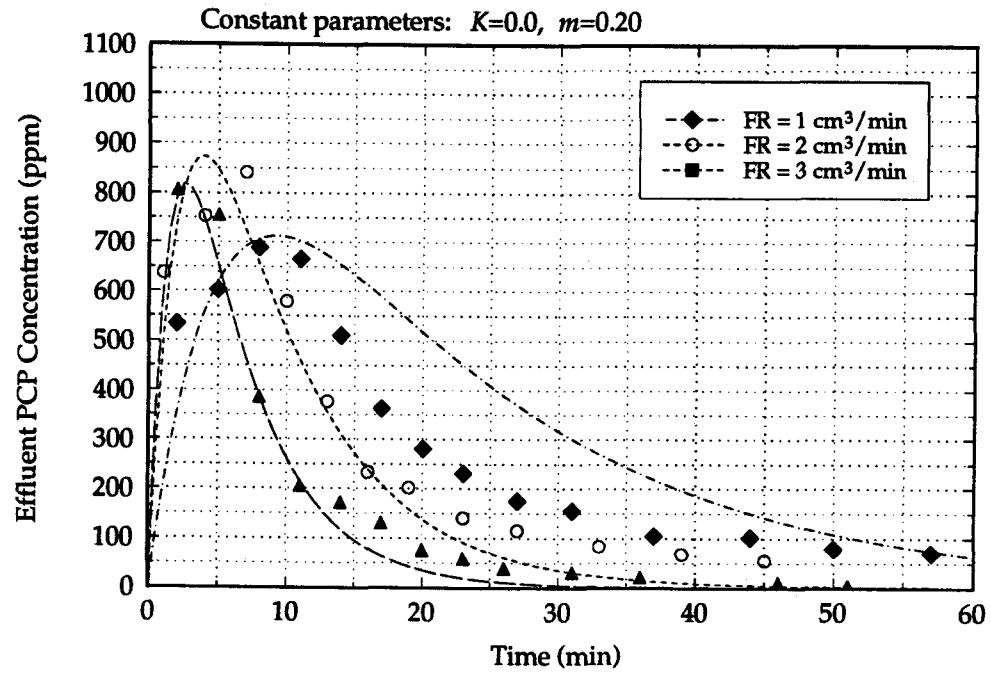
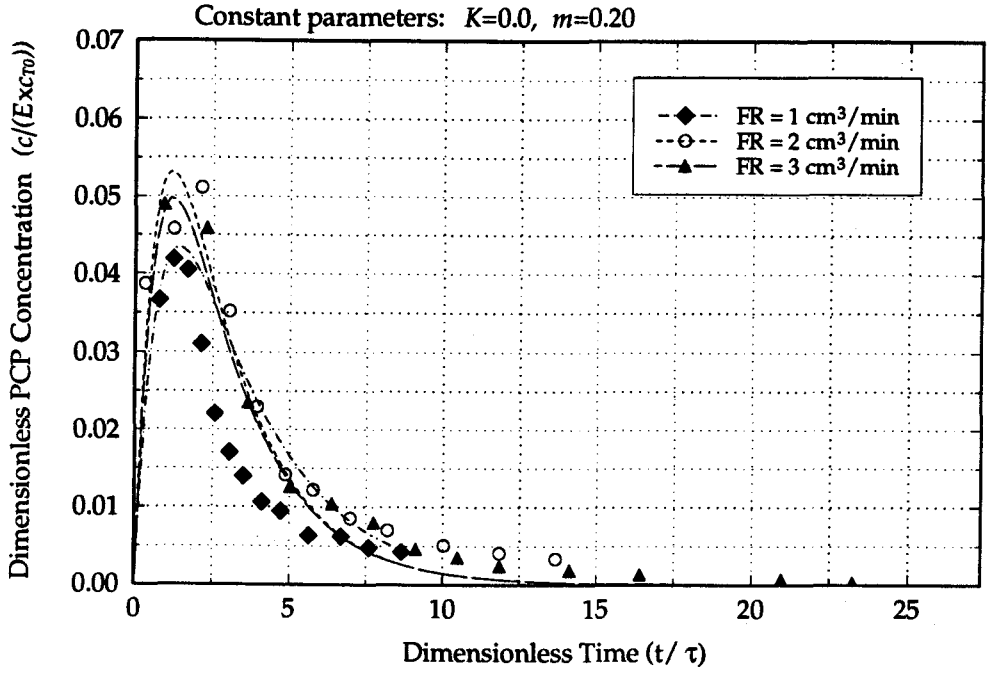
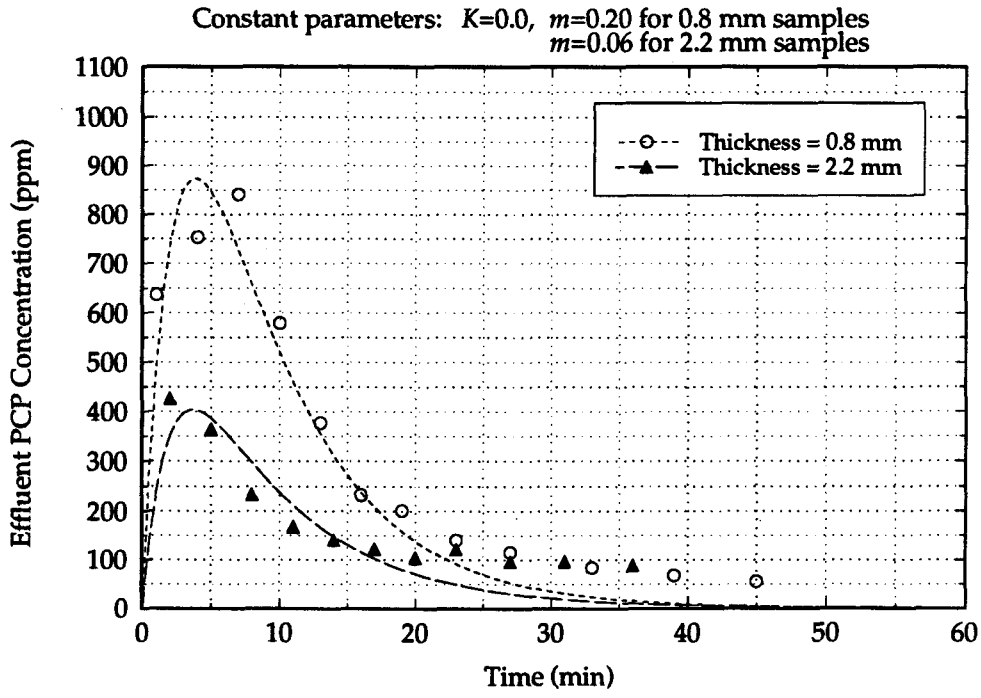


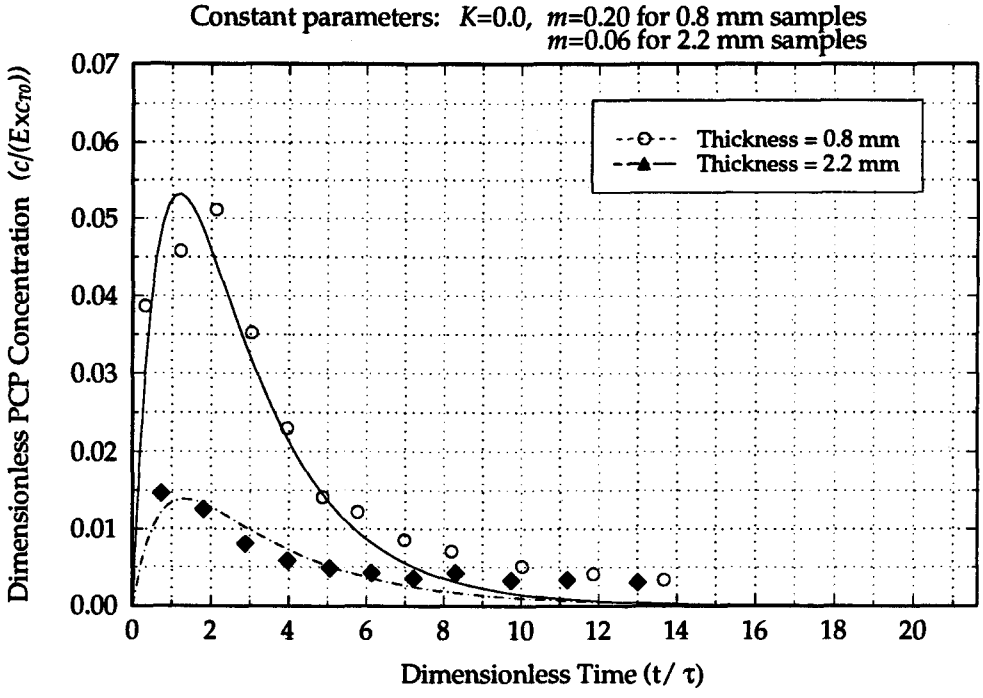
Figure 4-17. Best fit of PCP extraction histories using one model parameter for three temperatures at 22.5 MPa, 2 cm^3/min and 0.8 mm wafer thickness.





Figures 4-18a, 4-18b. Best fit of PCP extraction histories using one model parameter for three flow rates at 22.5 MPa, 353 K and 0.8 mm wafer thickness.





Figures 4-19a, 4-19b. Best fit of PCP extraction histories using one model parameter for two wafer thicknesses at 22.5 MPa, 353 K and 2 cm^3/min.

Srinivasan et al. (1990) obtained values of the combined mass transfer coefficient between 0.018/sec to 0.055/sec in the extraction of ethyl acetate from activated carbon using supercritical carbon dioxide as a solvent. Thus the combined mass transfer coefficients obtained from this work (0.0003 - 0.002/sec) are slightly lower than values in the literature for other SCFEs.

4.3.1 Pressure Effect on Combined Mass Transfer Coefficient

As shown in Figure 4-20, the values for the combined mass transfer coefficient increase as pressure increases. The bars in the Figures 4-20 to 4-23 show the 95% confidence intervals of estimated k_p values. Peker et al (1992) showed a similar tendency in caffeine extraction from water-soaked coffee beans. The combined mass transfer coefficient has a linear relationship over a range of pressures from 17.5 MPa to 22.5 MPa.

4.3.2 Temperature Effect on Combined Mass Transfer Coefficient

Figure 4-21 shows the values of the combined mass transfer coefficient estimated from the proposed mathematical model. The k_p values increase with temperature, which is similar to results in caffeine extraction (Peker et al., 1992) and ethyl acetate extraction (Srinivasan et al., 1990). Between 313 K to 333 K, k_p increased significantly. However, a further increase in temperature had little

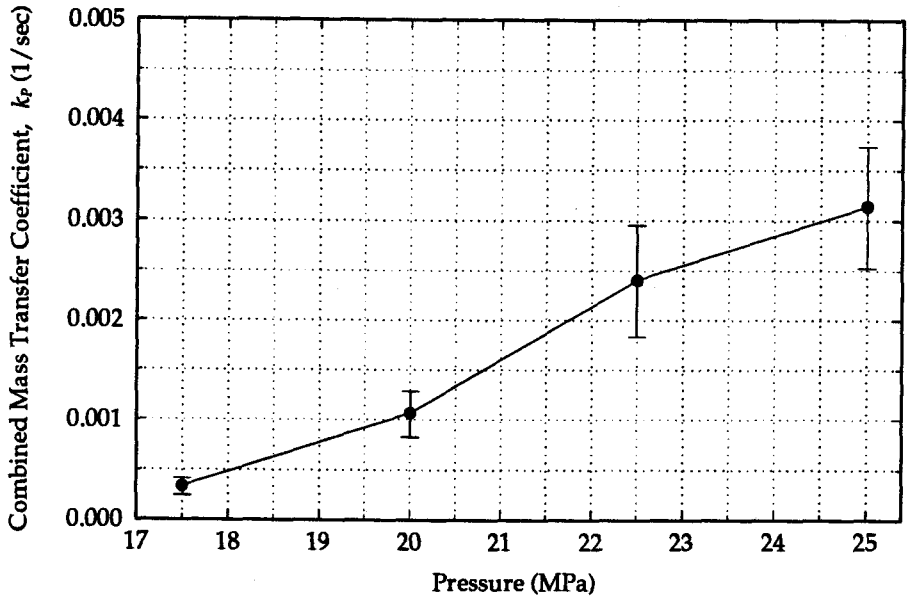


Figure 4-20. Pressure effect on combined mass transfer coefficient.

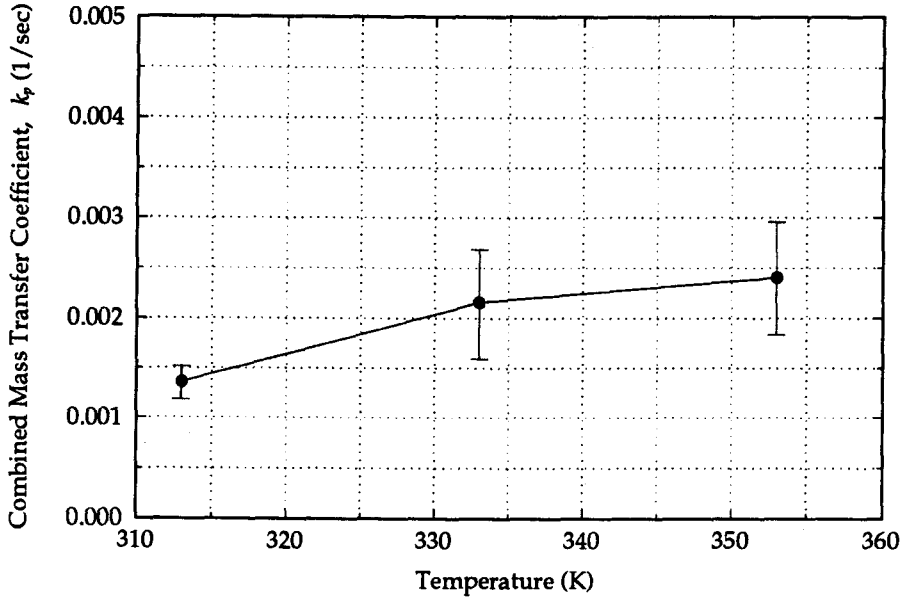


Figure 4-21. Temperature effect on combined mass transfer coefficient.

effect, as shown by similar ranges of 95 % confidence intervals for 333 K and 353 K.

4.3.3 Flow Rate Effect on Combined Mass Transfer Coefficient

Figure 4-22 shows that the combined mass transfer coefficient increased as the extraction flow rate increased. Figure 4-22 shows fitted values of the combined mass transfer coefficient versus the square root of flow rate. This relationship is motivated by conventional correlations for the convective mass transfer coefficient in the form of $Nu = f\ (Re^{1/2}Sc^{1/3})$. Dimensionless effluent concentration histories versus dimensionless time are plotted at different flow rates in Figure 4-18b. These data imply that an intermediate flow rate of 2 cm^3/min gives an optimum amount of PCP extraction per unit mass of solvent. At the lower flow rate, the mass transfer rate is slower, as shown in Figure 4-22. At higher flows mass transfer is faster, but less extraction per unit mass of solvent is obtained. A trade off between these two desirable attributes was also noted in other studies (Peker et al, 1992; Srinivasan et al,1990).

4.3.4 Sample Thickness Effect on Combined Mass Transfer Coefficient

Figure 4-23 shows the estimated values of combined mass transfer coefficient at two different sample thickness values. Those results are based on

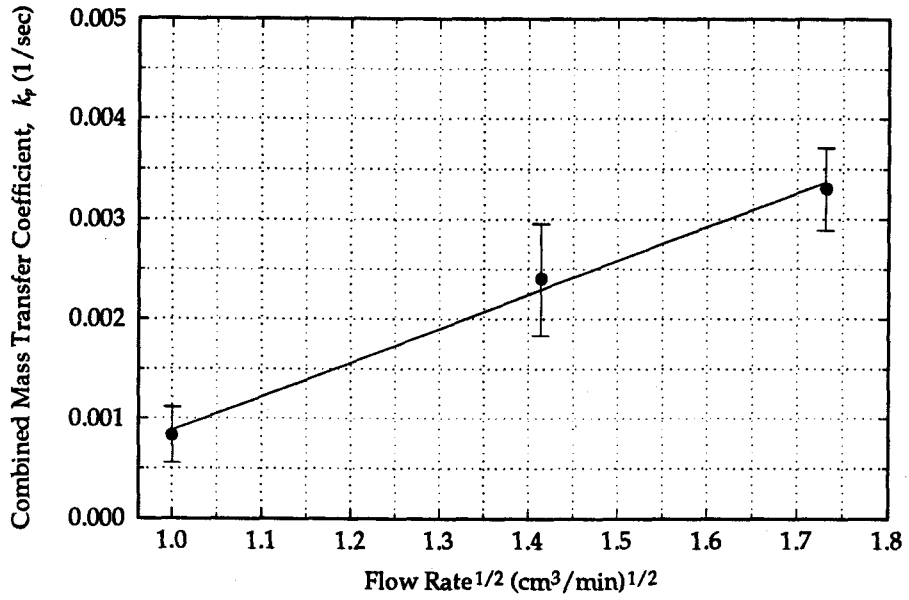


Figure 4-22. Flow rate effect on combined mass transfer coefficient.

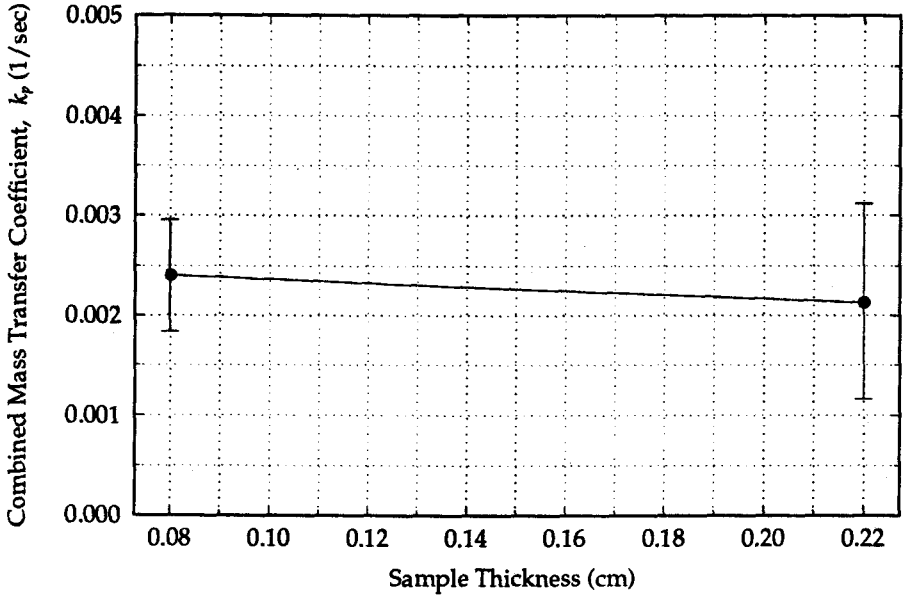


Figure 4-23. Sample thickness effect on combined mass transfer coefficient.

m = 0.20 and m = 0.06 for the fractional initial distribution of PCP in the pore fluid of wood wafers for 0.8 x 10 x 50 mm samples, and 2.2 x 10 x 50 mm samples, respectively. The 0.8 mm thickness samples had 23.07 Kg/m^3 of initial retention of PCP and 2.2 mm thickness samples had 35.86 Kg/m^3. There was a slight decrease of k_p value for the thicker samples, however the 95 % confidence intervals are pretty much overlapped. Therefore, no significant change in combined mass transfer coefficient was observed for the thicker wafers with higher initial loading of PCP.

The combined mass transfer coefficient depend on an effective diffusion coefficient and the convective mass transfer coefficient, as shown in Equation (20).

$$k_p = \frac{3k_f / (\frac{\delta}{2})}{3+Bi} \qquad (20)$$

where $Bi = k_f(\delta/2)/D_e$. The Biot number represents the ratio between external convective mass transfer and internal mass diffusion. Equation (20) can be considered for two extreme cases. One is the convective mass transfer limiting case ($Bi << 3$) and the other is effective diffusion limiting case ($Bi >> 3$). For the convective mass transfer limiting case, k_p simplifies to be proportional to k_f:

$$k_p = \frac{k_f}{(\frac{\delta}{2})} \qquad (34)$$

For the effective diffusion limiting case, k_p simplifies to be proportional to D_e:

$$k_p = \frac{3D_e}{(\frac{\delta}{2})^2} \qquad (35)$$

These limiting cases indicate that when diffusion is limiting the total mass transfer, more influence is excepted for sample thickness than when convective mass transfer is limiting. Since the data shown in Figure 4-23 do not show any significant effect due to sample size, more data for different sizes at the same initial loading of PCP should be obtained as another method of determining the dominant resistance to extraction at various operation conditions.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Supercritical solvent extraction of PCP from pressure treated wood was experimentally studied and mathematically analyzed. Following are the general conclusions from the present study:

(1) The experimental results are at least qualitatively described by the theoretical model, which includes desorption equilibrium, intraparticle diffusion, convective film mass transfer and an initial PCP distribution between cell lumen and cell wall. Quantitative agreement can be observed for the initial 30 minutes for extraction.

(2) During supercritical carbon dioxide extraction, the desorption rate of PCP from cell wall to cell lumen of wood wafer is very small compared to the rate of mass transfer from cell lumen to bulk volume of the extractor.

(3) The rate of extraction increased with pressure, temperature and flow

rate, as shown in an increase of combined mass transfer coefficient. However, there was no significant change of combined mass transfer for the different wafer sizes: 8 x 10 x 50 mm or 2.2 x 10 x 50 mm.

5.2 Recommendation for Future Work

(1) Generally, supercritical fluid extraction performance can be improved when a cosolvent is used. The study of cosolvent effects in the extraction of PCP from pressure treated wood using supercritical carbon dioxide as a solvent is recommended.

(2) Based on this study, the effect of wood characteristics, such as moisture, initial retention, and wood species are recommended for further study to improved process understanding.

(2) Larger sized wafers or chips should be studied as more representative of solids used in commercial applications. Sets of different size wafers should be prepared with the same initial loading of PCP so that size is the only variable.

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APPENDICES

APPENDIX A : RAW DATA

Supercritical Fluid Extraction of PCP from Contaminated Wood									
(Calculation Sheet)									
Experimental Date : 5/14/93									
Extraction Conditions :					Wood Conditions :				
	P =		175	bar		Initial Retention =		3.264	wt%
	T =		80	C		Initial Weight =		2.28	g
	F.R. =		2	ml/min		Final Retention =		2.838	wt%
	Run Time =		1	hr		Final Weight =		1.49	g
	Modifier =		0	%		Collection Amount =		82	ml
	Temperature of Expanded CO2 =					27	C		
Analysis Date :5/18/93									
Calibration Equation	Conc = 5.51737+8.12175*10^-4(Area)								

#	S. T.	CO2 Volume (ml)			CO2	Area (avg)	PCP	Concentration (PPM)	
	(min)	Initial	Final	V.C	(g)		(g)	with Aceton	with CO2
1	1			847.8	1.5153	42230	0.000221	39.81552025	145.65
2	4			847.8	1.5153	43770	0.000228	41.06626975	150.22
3	7			847.8	1.5153	47500	0.000244	44.0956825	161.30
4	10			847.8	1.5153	52790	0.000268	48.39208825	177.02
5	14			847.8	1.5153	69560	0.000344	62.012263	226.83
6	17			847.8	1.5153	77160	0.000378	68.184793	249.40
7	20			847.8	1.5153	76080	0.000373	67.307644	246.19
8	24			847.8	1.5153	74360	0.000365	65.910703	241.08
9	27			847.8	1.5153	61760	0.000309	55.677298	203.66
10	30	52	890	838	1.4978	53830	0.000273	49.23675025	182.21
11	36	55	906	851	1.521	43910	0.000228	41.17997425	150.07
12	41	71	920	849	1.5175	30160	0.000166	30.012568	109.64
13	46	60	914	854	1.5264	23960	0.000138	24.977083	90.71
14	53	71	918	847	1.5139	22500	0.000132	23.7913075	87.12
15					0		0	0	0.00
outlet						216600	0.011783	181.434475	

Supercritical Fluid Extraction of PCP from Contaminated Wood									
(Calculation Sheet)									
Experimental Date : 5/13/93									
Extraction Conditions :					Wood Conditions :				
	P =		200	bar		Initial Retention =		3.264	wt%
	T =		80	C		Initial Weight =		2.34	g
	F.R. =		2	ml/min		Final Retention =		2.103	wt%
	Run Time =		1	hr		Final Weight =		1.55	g
	Modifier =		0	%		Collection Amount =		55	ml
	Temperature of Expanded CO2 =					19	C		
Analysis Date : 5/17/93									
Calibration Equation :	Conc = 9.30677+7.90016*10^-4(Area)								

#	S. T.	CO2 Volume (ml)			CO2	Area (avg	PCP	Concentration (PPM)	
	(min)	Initial	Final	V.C	(g)		(g)	with Aceton	with CO2
1	1			880.2	1.6163	125800	0.000603	108.6907828	372.67
2	4			880.2	1.6163	150800	0.000712	128.4411828	440.36
3	9			880.2	1.6163	191800	0.000892	160.8318388	551.35
4	13			880.2	1.6163	119300	0.000574	103.5556788	355.07
5	18			880.2	1.6163	83000	0.000415	74.878098	256.76
6	21			880.2	1.6163	36300	0.000211	37.9843508	130.27
7	24			880.2	1.6163	46850	0.000257	46.3190196	158.85
8	29			880.2	1.6163	38140	0.000219	39.43798024	135.25
9	33	20	900	880	1.616	31050	0.000188	33.8367668	116.07
10	40	50	940	890	1.6343	21900	0.000148	26.6081204	90.25
11	44	75	950	875	1.6068	17520	0.000128	23.14785032	79.86
12	48	98	965	867	1.5921	15240	0.000118	21.34661384	74.33
13	55	70	959	889	1.6325	0	0	0	0.00
14				0	0	0	0	0	0.00
15					0		0	0	0.00
outlet						507100	0.017856	409.9238836	

Supercritical Fluid Extraction of PCP from Contaminated Wood									
(Calculation Sheet)									
Experimental Date : 5/15/93									
Extraction Conditions :					Wood Conditions :				
	P =		225	bar		Initial Retention =		3.264	wt%
	T =		80	C		Initial Weight =		2.22	g
	F.R. =		2	ml/min		Final Retention =		1.545	wt%
	Run Time =		1	hr		Final Weight =		1.37	g
	Modifier =		0	%		Collection Amount =		81	ml
	Temperature of Expanded CO2 =					24	C		
Analysis Date :5/18/93, 5/19									
Calibration Equation :			Conc = 10.8736+7.84058*10^-4(Area) for 1-9						
			Conc = 5.51737+8.12175*10^-4(area) for 10-13						

#	S. T.	CO2 Volume (ml)			CO2	Area (avg)	PCP	Concentration (PPM)	
	(min)	Initial	Final	V.C	(g)		(g)	with Aceton	with CO2
1	1			930.2	1.67939	232300	0.00107	193.0102734	636.76
2	4			930.2	1.67939	277300	0.00127	228.2928834	753.07
3	7			930.2	1.67939	311400	0.00141	255.0292612	841.19
4	10			930.2	1.67939	210000	0.00097	175.52578	579.11
5	13			930.2	1.67939	132000	0.00063	114.369256	377.41
6	16			930.2	1.67939	76160	0.00039	70.58745728	232.97
7	19			930.2	1.67939	63940	0.00034	61.00626852	201.35
8	23			930.2	1.67939	40480	0.00024	42.61226784	140.65
9	27	40	970	930	1.67903	30890	0.00019	35.09315162	115.86
10	33	35	968	933	1.68445	24610	0.00014	25.50499675	83.94
11	39	48	980	932	1.68264	18670	0.00011	20.68067725	68.13
12	45	50	980	930	1.67903	13870	9.3E-05	16.78223725	55.41
13	52	54	980	926	1.67181	0	0	0	0.00
14				0	0	0	0	0	0.00
15					0		0	0	0.00
outlet						372000	0.01974	307.64647	

Supercritical Fluid Extraction of PCP from Contaminated Wood									
(Calculation Sheet)									
Experimental Date : 5/20/93									
Extraction Conditions					Wood Conditions :				
	P =		250	bar		Initial Retention =		3.264	wt%
	T =		80	C		Initial Weight =		2.31	g
	F.R. =		2	ml/min		Final Retention =		1.362	wt%
	Run Time =		1	hr		Final Weight =		1.5	g
	Modifier =		0	%		Collection Amount =		84	ml
	Temperature of Expanded CO2 =					27	C		
Analysis Date :5/22/93, 5/24/93									
Calibration Equation :			Conc = 10.7016+7.73035*10^-4(Area)						
			Conc = 9.46657+7.35406*10^-4(Area) for 3, 4						

#	S. T.	CO2 Volume (ml)			CO2	Area (avg)	PCP	Concentration (PPM)	
	(min)	Initial	Final	V.C	(g)		(g)	with Aceton	with CO2
1	2			991.3	1.7717	337800	0.00151	271.832823	849.89
2	5			991.3	1.7717	411000	0.00182	328.418985	1026.62
3	8			991.3	1.7717	271000	0.00116	208.761546	652.82
4	11			991.3	1.7717	123400	0.00056	100.2156204	313.49
5	15			991.3	1.7717	84300	0.00042	75.8684505	237.35
6	19			991.3	1.7717	44330	0.00025	44.97024155	140.70
7	23			991.3	1.7717	39830	0.00023	41.49158405	129.82
8	26			991.3	1.7717	28160	0.00018	32.4702656	101.59
9	31			991.3	1.7717	16820	0.00013	23.7040487	74.17
10	35	25	1015	990	1.7695	0	0	0	0.00
11	42	21	1015	994	1.7766	14460	0.00012	21.8796861	68.27
12	48	45	1035	990	1.7695	0	0	0	0.00
13	54	49	1040	991	1.7713	0	0	0	0.00
14				0	0	0	0	0	0.00
15					0		0	0	0.00
								5/25 analysis	
outlet						375500	0.01851	278.2849565	

Supercritical Fluid Extraction of PCP from Contaminated Wood

(Calculation Sheet)

Experimental Date : 5/21/93 - 1

Extraction Conditions			Wood Conditions :		
P =	225	bar	Initial Retention =	3.264	wt%
T =	40	C	Initial Weight =	2.4	g
F.R. =	2	ml/min	Final Retention =	1.783	wt%
Run Time =	1	hr	Final Weight =	1.6	g
Modifier =	0	%	Collection Amount =	82	ml
Temperature of Expanded CO2 =			26	C	

Analysis Date : 5/24/93

Calibration Equation : Conc = 9.46652+7.35406*10^-4(Area)

#	S. T.	CO2 Volume (ml)			CO2	Area (avg)	PCP	Concentration (PPM)	
	(min)	Initial	Final	V.C	(g)		(g)	with Aceton	with CO2
1	2			1001	1.7951	230500	0.000992	178.977603	552.44
2	5			1001	1.7951	254400	0.00109	196.5538064	606.66
3	8			1001	1.7951	225500	0.000972	175.300573	541.10
4	11			1001	1.7951	181000	0.00079	142.575006	440.13
5	15			1001	1.7951	127700	0.000573	103.3778662	319.17
6	18			1001	1.7951	98560	0.000454	81.94813536	253.02
7	21			1001	1.7951	74600	0.000357	64.3278076	198.63
8	24			1001	1.7951	52550	0.000267	48.1121053	148.57
9	27			1001	1.7951	41800	0.000223	40.2064908	124.16
10	30			1001	1.7951	34520	0.000193	34.85273512	107.63
11	34	28	1030	1002	1.7969	27710	0.000165	29.84462026	92.07
12	39	33	1035	1002	1.7969	26740	0.000162	29.13127644	89.87
13	45	40	1040	1000	1.7933	19540	0.000132	23.83635324	73.68
14	53	35	1035	1000	1.7933	16790	0.000121	21.81398674	67.43
15					0		0	0	0.00
								5/25 analysis	
outlet						303600	0.0147	226.3484948	

Supercritical Fluid Extraction of PCP from Contaminated Wood											
(Calculation Sheet)											
Experimental Date : 5/21/93 -2											
Extraction Conditions					Wood Conditions :						
	P =		225	bar		Initial Retention =		3.264	wt%		
	T =		60	C		Initial Weight =		2.37	g		
	F.R. =		2	ml/min		Final Retention =		1.901	wt%		
	Run Time =		1	hr		Final Weight =		1.63	g		
	Modifier =		0	%		Collection Amount =		83	ml		
	Temperature of Expanded CO2 =					27.6	C				
Analysis Date : 5/25/93											
Calibration Equation :	Conc = 7.04516+7.22343*10^-4(Area)										

#	S. T.	CO2 Volume (ml)			CO2	Area (avg)	PCP	Concentration (PPM)	
	(min)	Initial	Final	V.C	(g)		(g)	with Aceton	with CO2
1	2			969.8	1.72983	283600	0.00117	211.9016348	678.67
2	5			969.8	1.72983	331700	0.00137	246.6463331	789.86
3	8			969.8	1.72983	182400	0.00077	138.8005232	444.65
4	11			969.8	1.72983	132400	0.00057	102.6833732	328.99
5	14			969.8	1.72983	74220	0.00034	60.65745746	194.37
6	18			969.8	1.72983	53580	0.00025	45.74829794	146.60
7	21			969.8	1.72983	44760	0.00022	39.37723268	126.19
8	25			969.8	1.72983	28240	0.00015	27.44412632	87.95
9	28			969.8	1.72983	22580	0.00013	23.35566494	74.85
10	32	39	1005	966	1.72314	15130	1E-04	17.97420959	57.83
11	38	20	988	968	1.72671	14800	9.8E-05	17.7358364	56.94
12	44	45	1020	975	1.7392	13890	9.5E-05	17.07850427	54.44
13	50	60	1030	970	1.73028				
14									
15					0		0	0	0.00
outlet						327300	0.016	243.4680239	

Supercritical Fluid Extraction of PCP from Contaminated Wood

(Calculation Sheet)

Experimental Date : 5/28/93 -2

Extraction Conditions			Wood Conditions :		
P =	225	bar	Initial Retention =	3.26	wt%
T =	80	C	Initial Weight =	2.37	g
F.R. =	1	ml/min	Final Retention =	1.83	wt%
Run Time =	1	hr	Final Weight =	1.66	g
Modifier =	0	%	Collection Amount =	105	ml
Temperature of Expanded CO2 =			25	C	

Analysis Date : 6/1/93, 5/31/93

Calibration Equation : Conc = 7.70949+7.52309*10^-4(Area) for 1-9

Conc = 8.7572+7.59939*10^-4(area) for 10-14

#	S. T.	CO2 Volume (ml)			CO2	Area (avg)	PCP	Concentration (PPM)	
	(min)	Initial	Final	V.C	(g)		(g)	with Aceton	with CO2
1	2			964.8	1.73602	211800	0.000926	167.0485362	533.19
2	5			964.8	1.73602	240600	0.001046	188.7150354	602.30
3	8			964.8	1.73602	276600	0.001196	215.7981594	688.68
4	11			964.8	1.73602	267100	0.001157	208.6512239	665.89
5	14			964.8	1.73602	202500	0.000887	160.0520625	510.87
6	17			964.8	1.73602	140800	0.00063	113.6345972	362.76
7	20			964.8	1.73602	106600	0.000487	87.9056294	280.65
8	23			964.8	1.73602	85620	0.0004	72.12218658	230.27
9	27			964.8	1.73602	62710	0.000304	54.88678739	175.25
10	31	45	1010	965	1.73638	52730	0.000271	48.82878347	155.88
11	37	20	989	969	1.74357	31930	0.000183	33.02205227	104.99
12	44	60	1025	965	1.73638	30710	0.000178	32.09492669	102.46
13	50	19	980	961	1.72918	20810	0.000136	24.57153059	78.77
14	57	16	980	964	1.73458	17480	0.000122	22.04093372	70.44
15					0		0	0	0.00
outlet						164900	0.011149	134.0711411	

Supercritical Fluid Extraction of PCP from Contaminated Wood

(Calculation Sheet)

Experimental Date : 8/2/93-2

Extraction Conditions			Wood Conditions :		
P =	225	bar	Initial Retention =	3.26	wt%
T =	80	C	Initial Weight =	2.38	g
F.R. =	3	ml/min	Final Retention =	1.90	wt%
Run Time =	1	hr	Final Weight =	1.49	g
Modifier =	0	%	Collection Amount =	85	ml
Temperature of Expanded CO2 =			37	C	

Analysis Date : 8/5/93

Calibration Equation : Conc = -7.42504+8.48887*10^-4(Area)

#	S. T.	CO2 Volume (ml)			CO2	Area (avg	PCP	Concentration (PPM)	
	(min)	Initial	Final	V.C	(g)		(g)	with Aceton	with CO2
1	2			957	1.65532	292500	0.001335	240.8744075	806.08
2	5			957	1.65532	274600	0.001251	225.6793302	755.27
3	8			957	1.65532	144700	0.00064	115.4089089	386.38
4	11			957	1.65532	81100	0.000341	61.4196957	205.66
5	14			957	1.65532	69200	0.000285	51.3179404	171.84
6	17			957	1.65532	54980	0.000218	39.24676726	131.43
7	20			957	1.65532	35400	0.000125	22.6255598	75.77
8	23			957	1.65532	29400	9.72E-05	17.5322378	58.72
9	26			957	1.65532	22600	6.52E-05	11.7598062	39.38
10	31	20	980	960	1.66051	19630	5.12E-05	9.23861181	30.84
11	36	15	975	960	1.66051	16570	3.68E-05	6.64101759	22.17
12	41	20	975	955	1.65186				
13	46	20	975	955	1.65186	12660	1.84E-05	3.32186942	11.15
14	51	20	975	955	1.65186	10230	6.98E-06	1.25907401	4.23
15					0		0	0	0.00
outlet							0.00447	618.194679	

Supercritical Fluid Extraction of PCP from Contaminated Wood

(Calculation Sheet)

Experimental Date : 6/22/93

Extraction Conditions			Wood Conditions :	(2.2mm thickness samples)	
P =	225	bar	Initial Retention =	3.69	wt%
T =	80	C	Initial Weight =	4.13	g
F.R. =	2	ml/min	Final Retention =	1.69	wt%
Run Time =	1	hr	Final Weight =	2.77	g
Modifier =	0	%	Collection Amount =	85	ml
Temperature of Expanded CO2 =			26	C	

Analysis Date : 6/24/93

Calibration Equation : Conc = 17.5817+7.12486*10^-4(Area)

#	S. T.	CO2 Volume (ml)			CO2	Area (avg	PCP	Concentration (PPM)	
	(min)	Initial	Final	V.C	(g)		(g)	with Aceton	with CO2
1	2			950.2	1.70403	159300	0.000727	131.0807198	426.29
2	5			950.2	1.70403	132600	0.000621	112.0573436	364.44
3	8			950.2	1.70403	76340	0.000399	71.97288124	234.11
4	11			950.2	1.70403	48030	0.000287	51.80240258	168.51
5	14			950.2	1.70403	36340	0.000241	43.47344124	141.42
6	17			950.2	1.70403	28310	0.000209	37.75217866	122.81
7	20			950.2	1.70403	20410	0.000178	32.12353926	104.50
8	23			950.2	1.70403	27810	0.000207	37.39593566	121.65
9	27			950.2	1.70403	16580	0.000163	29.39471788	95.63
10	31	30	985	955	1.71264	17240	0.000166	29.86495864	96.67
11	36	60	1010	950	1.70367	13520	0.000151	27.21451072	88.55
12	42	20	969	949	1.70188		0		
13	48	20	967	947	1.69829		0		
14	55	20	970	950	1.70367		0		
15					0		0	0	0.00
outlet									

APPENDIX B : COMPUTER PROGRAM

```
C       SCFEXT.FOR
C       THIS PROGAM IS USED TO FIND OPTIMAL DESORPTION RATE
C       CONSTANT(PAR(1)), OVERALL MASS TRANSFER COEFFICIENT(PAR(2)),
C       AND INITIAL DISTRIBUTION COEFFICIENT(PAR(3)) TO FIT THE
C       CONCENTRATION HISTORY FOR THE SUPERCRITICAL FLUID PCP
C       EXTRACTION FROM CONTAMINATED WOOD WAFER.
C       THE MODEL EQUATION IS;
C
C
C                C0*PAR(3)*E*PAR(2)
C            F = ------------------------ (EXP(A1*T*X) - EXP(A2*T*X))
C                     P*(A1-A2)
C
C       WHERE
C                                                    4*PAR(2)
C                                   -B + (B**2 - ------------- )**0.5
C                                                  P+PAR(1)
C         A1(PAR(1), PAR(2)) =  ---------------------------------
C                                                    2
C
C
C                                                    4*PAR(2)
C                                   -B - (B**2 - ------------- )**0.5
C                                                  P+PAR(1)
C         A2(PAR(1), PAR(2)) =  ---------------------------------
C                                                    2
C
C
C                                          1
C         B(PAR(1), PAR(2)) = 1 + ( ------------- + E)*PAR(2)
C                                       P+PAR(1)
C
C         PAR(1) = DESORPTION RATE CONSTANT.
C         PAR(2) = OVERALL MASS TRANSFER COEFFICIENT.
C         PAR(3) = INITIAL DISTRIBUTION COEFFICIENT.
C         E = (N*L*W*DELTA/BULK VOLUME OF EXTRACTOR).
C         P = POROSITY OF WOOD WAFER.
C         C0 = INITIAL PCP CONCENTRATION OF WOOD WAFER.
C         X = DIMENSIONLESS TIME (TIME/RESIDUAL TIME).
C         T = RESIDUAL TIME
C
C
C       @@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
C         MAIN PROGRAM
C       @@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
        IMPLICIT DOUBLE PRECISION (A-H, O-Z)
        CHARACTER*10 NFILE
        INTEGER NOB, NPAR, ISC(100), NSC, NP, NT, NF, NTH
        REAL X(50), OBS(50), PAR(3), SC(150), RT, E, C0
        COMMON /CON/RT, E, C0
        COMMON //X, OBS
C
C            read observed function values and independent varibales
1000    WRITE(*,*) 'ENTER THE DATA FILE NAME'
        READ(*, 100) NFILE
        OPEN (1, FILE=NFILE, STATUS='OLD')
        REWIND (1)
        READ(1, 110) NP, NT, NF, NTH, NOB, NPAR
```

```
      DO 10 I = 1, NOB
         READ (1, 120) X(I), OBS(I)
10    CONTINUE
      CLOSE(1)
C
C
C        calculation of constants
      NSC = 6+2*NOB+NPAR*(17+2*NPAR+NOB)
      IF(NTH.EQ.1) THEN
         RT = 6.583/NF
         E = 0.504
         C0 = 0.0326
      ELSE IF(NTH.EQ.2) THEN
            RT = 5.543/NF
            E = 0.787
            C0 = 0.0372
        END IF
C
C
C         read the initial guesses
      WRITE(*,*) '  PARAMETER 1 = ADSORPTION COEFFICIENT'
      WRITE(*,*) '  PARAMETER 2 = OVERALL MASS TRANSFER
     *  COEFFICIENT'
      WRITE(*,*) '  PARAMETER 3 = INITIAL DISTRIBUTION
     *  COEFFICIENT'
      WRITE(*,*)
      WRITE(*,*) 'ENTER THE INITIAL GURSS OF PARAMETER 1'
      READ(*,*) PAR(1)
      WRITE(*,*) 'ENTER THE INITIAL GUESS OF PARAMETER 2'
      READ(*,*) PAR(2)
      WRITE(*,*) 'ENTER THE INITIAL GUESS OF PARAMETER 3'
      READ(*,*) PAR(3)
C
C
C        call LS
      CALL LSGEN (NOB, OBS, NPAR, PAR, ISC, SC, NSC)
C
C
C         print the outputs
      WRITE (*, 130) PAR(1)
      WRITE (*, 140) PAR(2)
      WRITE (*, 150) PAR(3)
C
C
C         data creation
      WRITE (*, *) 'DO YOU WANT TO SAVE THE MODEL PREDICTION ?'
      WRITE (*, *) ' ( YES = 1,   NO = 2 ) '
      READ (*, *) NS
      IF (NS.NE.1) GO TO 2000
      CALL MODATA (PAR, F, NOB, NPAR, NP, NT, NF, NTH)
C
C
C        termination
      WRITE (*, *) 'DO YOU WANT TO CONTINUE ? (YES = 1, NO = 2)'
      READ (*, *) NN
      IF (NN.EQ.1) GO TO 1000
C
C
C         formats
100   FORMAT (A)
110   FORMAT (//29X, I5, /29X, I5, /29X, I5, /29X, I5,
     *  //25X, I5, /25X, I5, //)
```

```
120     FORMAT (5X, F10.4, 5X, F10.4)
130     FORMAT ('PAR(1) =', 5X, F15.8)
140     FORMAT ('PAR(2) =', 5X, F15.8)
150     FORMAT ('PAR(3) =', 5X, F15.8)
C
C
2000    STOP
        END
C
C
C       @@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
C         SUBROUTINE MODEL
C       @@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
        SUBROUTINE MODEL(PAR, F, NOB, NPAR)
        IMPLICIT DOUBLE PRECISION (A-H, O-Z)
        REAL  PAR(3), F(50), X(50), OBS(50), B, A1, A2, RT, E, C0
        COMMON /CON/RT, E, C0
        COMMON //X, OBS
C
*       WRITE(*, 100) PAR(1), PAR(2), PAR(3)
        DO 10 I = 1, NOB
        B = 1+(1/(0.73+PAR(1))+E)*PAR(2)
        A1 = (-B+(B**2-4*PAR(2)/(0.73+PAR(1)))**0.5)/2
        A2 = (-B-(B**2-4*PAR(2)/(0.73+PAR(1)))**0.5)/2
        F(I)=EXP(A1*X(I)/RT)-EXP(A2*X(I)/RT)
        F(I)=(C0*(10**6)*E*PAR(2)*PAR(3)/(0.73*(A1-A2)))*F(I)
*        WRITE(*, 110) X(I), F(I)
10      CONTINUE
C
100     FORMAT(//5X,'ESTIMATED PARAMETERS:',
     *   /15X,'ADSORPTION COEFFICIENT =',F15.8,
     *   /15X,'MASS TRANSFER COEFFICIENT =', F15.8,
     *   /15X,'INITIAL PARTITION COEFFICIENT =', F15.8)
110     FORMAT (10X, F10.4, 10X, F10.4)
        RETURN
        END
C
C
C       @@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
C         SUBROUTINE MODATA
C       @@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
C       THIS SUBROUTINE IS USED TO CREAT THE DATA FILE FROM THE
C       ESTIMATION.
C
        SUBROUTINE MODATA(PAR, F, NOB, NPAR, NP, NT, NF, NTH)
        IMPLICIT DOUBLE PRECISION (A-H, O-Z)
        CHARACTER*10 NMODOUT
        REAL  PAR(3), F(200), X(200), B, A1, A2, RT, E, C0
        COMMON /CON/RT, E, C0
C
        WRITE(*,*) 'ENTER THE MODEL DATA OUTPUT FILE NAME'
        READ(*, 100) NMODOUT
C
        OPEN (2, FILE=NMODOUT, STATUS='NEW')
        WRITE(2, 110) NP, NT, NF, NTH
        WRITE(2, 120) PAR(1), PAR(2), PAR(3)
        WRITE(2, 130)
        X(1) = 0.0
        DO 10 I = 1, 121
        B = 1+(1/(0.73+PAR(1))+E)*PAR(2)
        A1 = (-B+(B**2-4*PAR(2)/(0.73+PAR(1)))**0.5)/2
        A2 = (-B-(B**2-4*PAR(2)/(0.73+PAR(1)))**0.5)/2
```

```
      F(I)=EXP(A1*X(I)/RT)-EXP(A2*X(I)/RT)
      F(I)=(C0*(10**6)*E*PAR(2)*PAR(3)/(0.73*(A1-A2)))*F(I)
      WRITE(2, 140) X(I), F(I)
      X(I+1) = X(I) + 0.5
10    CONTINUE
      CLOSE(2)
C
100   FORMAT (A)
110   FORMAT(//5X,'CONDITIONS:', /15X,'PRESSURE =',I5,'BAR',/15X,
     * 'TEMPERATURE =',I5,'C',/15X,'FLOW RATE =',I5,'ml/min',/15X,
     * 'SAMPLE THICKNESS =',I5)
120   FORMAT(//5X,'ESTIMATED PARAMETERS:',
     *  /15X,'ADSORPTION COEFFICIENT =',F15.8,
     *  /15X,'MASS TRANSFER COEFFICIENT =', F15.8
     *  /15X,'INITIAL PARTITION COEFFICIENT =', F15.8)
130   FORMAT(//5X,'MODEL OUTPUT
     *  DATA',/13X,'TIME',12X,'CONCENTRATION')
140   FORMAT (10X, F15.4, 10X, F15.4)
      RETURN
      END
```