# A SUPERCRITICAL EXTRACTION EXPERIMENT

## For the Unit Operations Laboratory

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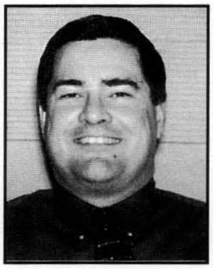
Supercritical fluid extraction (SCFE) is becoming a viable unit operation in the chemical process industry. It uses the distinguishing properties of a fluid that is above its critical point (critical temperature and pressure) to enhance performance in an extraction process. While the concept of SCFE has been known for over a century,[1] it has not been widely used in industry for a variety of reasons. Foremost among these reasons is the high financial risk involved with SCFE—specifically, high installation and operating costs for a process with a relatively short track record of commercial-scale success. Another reason is that a conventional separation technique is usually already available. Add to this the difficulties caused by the lack of sound theoretical models available for scale-up and it becomes obvious why there has been no incentive for SCFE development on a wide-scale industrial level. Even the early commercial applications, such as propane deasphalting in the 1930s, the SOLEXOL process of the 1940s, and the ROSE process in the 1950s, were not enough to generate large-scale interest.[2]

While these reasons remain true today, new motivating factors have recently paved the way for SCFE to become a viable extraction alternative. The modern chemical engineer is faced with environmental regulations that require strict control of emissions and reductions in hazardous waste. A change in energy costs has lessened the favorable gap in operating costs conventional high-heat separation techniques such as distillation have historically had over high-pressure SCFE systems. Increased performance demands, such as lower acceptable limits of either residual solvent or other contaminants in the food and pharmaceutical industries, have increased the popularity of SCFE. Also, SCFE solvents (such as carbon dioxide) are often more environmentally friendly.

As SCFE becomes more and more popular in industry, it is finding widespread applications from the decaffeination of coffee to the removal of trace organic contaminants in waste water.[3] Additional work is going on in many other areas from coal liquefaction[4] to fractionation and purification of polymers.[5] Some of these processes (such as coffee decaffeination) are vastly different from the original deasphalting and ROSE processes, while others (such as coal liquefaction) are very similar. While these widely varying applications are using many different solvents, the one used most predominantly is carbon dioxide.

Supercritical fluid extraction also presents a unique combination of high-pressure phase equilibrium and mass transfer. As such, an experiment dealing with SCFE represents a



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valuable addition to the traditional unit operations laboratory. With that in mind, this article discusses a laboratory experiment that both reinforces fundamental engineering principles and introduces the students to one segment of this growing technology—specifically solid/SCFE.

The experiment provides an opportunity for the students to explore SCFE and to use their engineering skills to deal with issues of scale-up and high-pressure equipment design and operation.[6] From a thermodynamic point of view, it allows students to explore physical-property prediction at high pressures far away from ideal behavior when experimental data are not available. They are then asked to use these predictions to correlate an equipment design parameter such as the mass transfer coefficient. Additionally, students have the opportunity to evaluate the usefulness of the data they have collected. They will need to understand that if the data indicates saturation of the exit stream, their analysis of the mass transfer coefficient will be invalid because the equation they are using (see Eq. 1 in the "Analysis" section) becomes indeterminate. Finally, they will need to have developed a plan to avoid saturation prior to starting the experiment in order to be successful.

As far as we know, the inclusion of a supercritical extraction experiment in the senior unit operations laboratory is unique.

## STUDENT EXPERIMENT

The experiment consists of a semi-continuous packed-bed extraction of naphthalene by supercritical carbon dioxide. The primary objective is to measure the mass transfer coefficient for the extraction at a variety of conditions and to develop a correlation for it as a function of these process conditions. Carbon dioxide was the chosen solvent because of its moderate critical conditions (304.2 K, 73.8 bar), its widespread industrial use, and its environmentally friendly nature. It is also nontoxic, making it a very safe lab solvent. Naphthalene was chosen because of its relatively high solubility in supercritical carbon dioxide and the availability of sufficient data on the system.[5]

### *Equipment*

The experiment consists primarily of a supercritical screening system (see Figure 1) designed and manufactured by Autoclave Engineers of Erie, Pennsylvania. The pre-as-

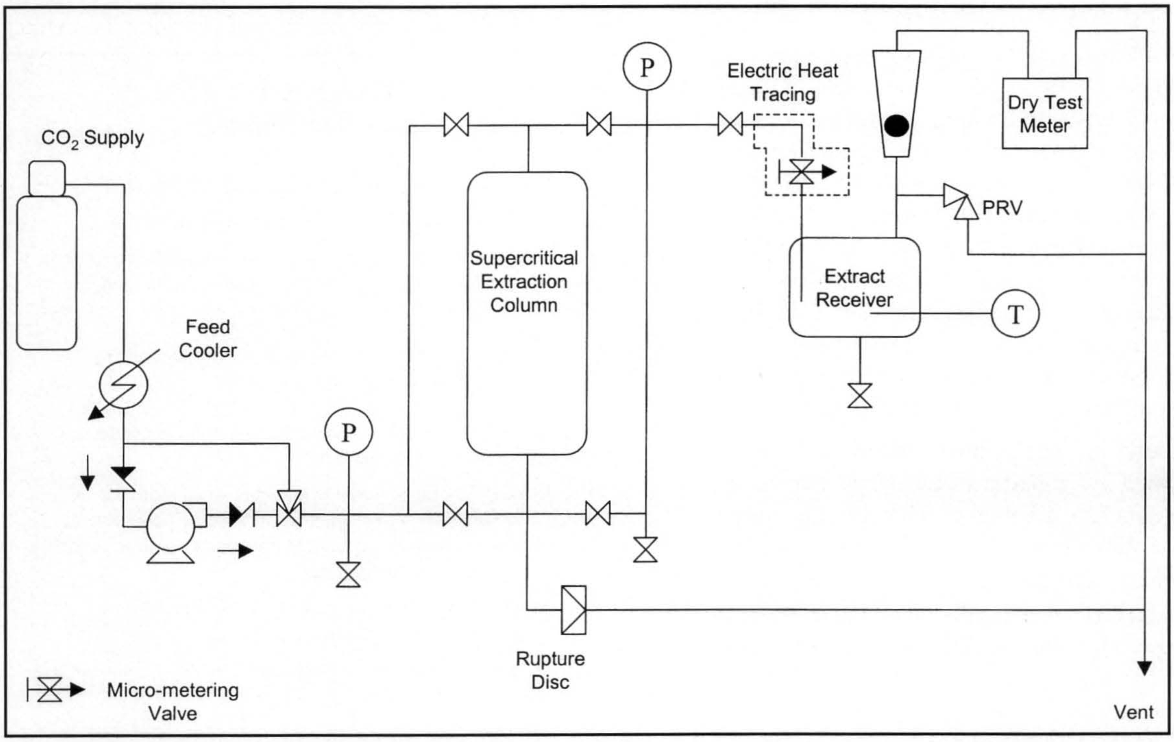

***Figure 1.*** *Flow diagram: supercritical fluid extraction system.*

sembled system includes all the necessary basic components: feed pump, extraction column, extract receiver, instrumentation, and a heated pressure boundary used to depressurize the exit stream. The cost of an Autoclave (814-838-5700) system typical of the one used in this laboratory was slightly lower than a similar system made by ISCO (800-228-4250). The heated pressure boundary was optional and added to the cost of the ISCO SCF 1200 system. One additional benefit of the Autoclave system is that it is a little larger in size than the ISCO system. Since this is intended to be a unit operations laboratory, we felt that having an analytical-scale unit would not do justice to the concept of SCFE as a unit operation. We wanted the students to have some degree of a "hands-on" experience with the lab that we felt would not be achieved with smaller analytical-scale equipment.

A standard $CO_2$ cylinder with a liquid dip tube is used as the feed tank. The $CO_2$ is cooled by passing the feed tube through an ice bath prior to entering a Milton Roy 1/4-Hp, variable-speed positive-displacement (PD) pump. The PD pump is capable of operating between 40-400 cc/hr. The pump discharge pressure is controlled by an adjustable back-pressure control valve that can operate in the range of 8-480 bar. Excess flow, which causes a pressure higher than the desired set point, is recirculated back to the suction side of the pump. The pump discharge pressure is measured just upstream of this control valve. A vapor vent valve is supplied downstream of the back-pressure control valve. This allows any vaporized $CO_2$ caught in the pump feed line to be vented off during start-up. Without the vent, the feed pump would become vapor bound and cavitate. Additional cooling is obtained by packing the pump head in ice.

Four valves around the extraction column isolate the column and provide the flexibility needed to operate it in either an upflow or downflow configuration. The column is 12 inches long, has an inside diameter of 0.688 inches (nominal 1 inch OD), and is rated for approximately 700 bar at 100°C. It can be electrically heated with two external band heaters. A surface-mounted thermocouple measures the outer column wall temperature, and a Watlow proportional/integral controller is used to control the temperature. The column is protected from overpressurization by a 1/4-inch diameter rupture disc that is piped directly to the bottom of the column. The disc is nominally rated for 480 bar at 22°C.

The pressure boundary on the downstream side of the column is maintained by a micro-metering needle valve, also supplied by Autoclave Engineers. The column can be isolated upstream of this valve with a blocking valve. The discharge lines from the column, as well as the body of the micro-metering valve, are electrically heat traced with a 110-volt heating tape. The heat tracing is in place to counteract the large Joule-Thomson cooling effect that results when the $CO_2$ flashes across the micro-metering valve and to prevent the line from freezing.

The extracted material is collected in the extract receiver. This vessel has a nominal volume of 99 cubic centimeters and has a drain valve at the bottom. The vessel is protected by a pressure relief valve set to open at 1.4 bar (at 22°C). The extract and solvent enter the receiver from the top. The extract, which is no longer soluble in the non-supercritical solvent, separates from the solvent and is collected in the vessel while the solute-free $CO_2$ is discharged from the top of the vessel. It then passes through a small filter to a rotameter and then through the dry test meter. In addition, the temperature in the extract receiver is measured by a thermocouple. The rotameter (calibrated for $CO_2$ at standard temperature and pressure in units of standard cubic feet per minute) measures the instantaneous $CO_2$ flow rate. The $CO_2$ flow is then totalized by a dry test meter. This provides total standard cubic feet of $CO_2$ used during an experiment.

## *Procedure*

The students are provided with the equipment, and are given detailed safety instructions and a list of "Discussion Topics" (see Table 1). Additionally, the experiment is conducted under closer-than-normal supervision for the senior unit operations lab. The students must develop their own experimental plan that will allow them to answer the questions outlined in the discussion topics. In developing their plan, they must decide on the pressures at which to operate the column, whether to use upflow or downflow through the column, what flow rates to use, and how long each extraction should last to provide meaningful data.

An individual experiment consists of charging the extrac-

### TABLE 1
### Discussion Topics

1. Should the column exit stream be saturated with naphthalene?
2. Discuss how you evaluated the mass transfer coefficient, k.
3. For packed beds, the mass transfer coefficient is often represented as a function of the $N_{Re}$, $N_{Sc}$, and $N_{Gr}$ numbers, if that function takes the following form, determine the values of the constants a, b, c, and d.

$$\frac{k}{V^0} = a(N_{Re})^b (N_{Sc})^c (N_{Gr})^d$$

4. What is the fugacity coefficient of the solute in the condensed phase at its sublimation pressure?
5. Use the Peng-Robinson or other suitable equation of state to predict the solubility of the solute in the supercritical solvent. How well does the equation of state prediction compare to the solubility reported in the literature?
6. How much energy input is required to maintain isothermal conditions across the micro-metering valve?
7. Support your decision to operate the column in either the upflow or downflow configuration.

tion column with a known amount of naphthalene (filling the rest of the column void with sand), re-assembling the system, pressurizing the system to the desired operating pressure at a chosen temperature, and initiating flow of supercritical carbon dioxide. Periodic measurements of feed-pump and column pressure, column and extract-receiver temperature, and instantaneous and cumulative carbon-dioxide flow rates are taken.

Once each individual extraction is completed, the column is re-weighed to obtain the quantity of naphthalene extracted. The column, rather than the naphthalene recovered in the extract receiver, is weighed because it is difficult to account for all the naphthalene in the receiver without the addition of another solvent. Some naphthalene usually precipitates on the piping walls after the micro-metering valve assembly. (This needs to be cleaned out between each experimental run.) Given this, less error is introduced into the experiment by doing the simple loss-in-weight measurement on the column.

Safety is a key aspect of the laboratory for two reasons. First and foremost is to ensure the safety of the students performing the high-pressure experiment; second is the heightened appreciation for safety the students gain from completing a high-pressure experiment such as this. To perform this experiment safely, students are required to develop a level of proactive thinking that they are not typically required to have in other unit operations laboratory experiments (*i.e.,* fluid flow, efflux time of a tank, or pressure drop in a packed column). The students must evaluate all the possible outcomes of their actions prior to doing anything with the equipment to make sure that the desired result is obtained safely. Students are not allowed to operate the equipment until they have demonstrated reasonable safety awareness to the instructor. This is not to say that the previously mentioned experiments should be performed casually or unsafely, but rather that the chance for serious injury is greater when performing a high-pressure experiment such as SCFE. This creates an atmosphere in which the students take lab safety very seriously. Providing this heightened level of safety awareness was a significant underlying objective of the laboratory and was one of the key reasons this experiment (High-Pressure Supercriticial Extraction) was considered rather than something such as a simple wetted-wall mass-transfer experiment.

Some of the key safety instructions given to the students are

- *No work can be done on the extraction column or associated piping until the system has been depressurized and then verified. Verification of depressurization is accomplished by opening all valves around the column and making sure that* ***both*** *inlet and outlet pressure gauges read zero and that there is no discharge from either of the two vents. Even if the column discharge is plugged, the inlet pressure gauge should still read zero when the column is depressurized. If this state is not obtained, the students are required to obtain help from either the instreuctor or the teaching instructor in the lab.*
- *No work should be done on the extraction column while it is plumbed up and in place on the extraction unit. All work should be completed while the column is out of service and on the workbench. Additionally, step-by-step instructions for loading and unloading the extraction column are located in the appendix of the student laboratory.*
- *The maximum operating temperature set in the student laboratory is 55 °C. While this was done to make sure that the column operating pressure would not exceed design limits, it also prevents liquid naphthalene from being pushed out of the column because the 55 °C limit is significantly lower than the 80-82 °C naphthalene melting point.*

Finally, with regard to safety, the students should be made aware of the issue of retrograde condensation within SCF systems. This is the phenomenon that can occur when vapor-liquid equilibrium exists at a temperature or pressure above the mixture critical point. In such a situation, increasing the operating temperature at constant pressure may lead to condensation. This can be a problem in the student experiment where the micro-metering valve and discharge piping are electrically heat traced to prevent freezing. The students should be cautioned to use the heat tracing only to maintain isothermal conditions in this part of the system and not to add unnecessary heat. Should retrograde condensation occur at the inlet of the micro-metering valve, the possibility of the system being plugged increases and the system will need to be depressurized as outlined above in the first bullet. The naphthalene-$CO_2$ system is susceptible to retrograde condensation when the operating pressures are around 125 bar and below.

## Analysis

The first step in the analysis is for the students to ensure that the carbon dioxide exiting the column is not saturated with naphthalene (first discussion topic in Table 1). This could happen if either the naphthalene/sand ratio charged to the column is too large or if the carbon dioxide flow rate is too small. In these cases, the effective contact time may be long enough for saturation to occur. This, of course, would render any mass transfer coefficient calculations meaningless.

Students can then determine the mass transfer coefficient, k, from the well-known relationship

$$\frac{C_1 V^0}{Az} = k \Delta C_{LM} \tag{1}$$

where $C_1$ is the average naphthalene concentration in the exit stream (as determined by material balance), $V^0$ is the empty-column superficial velocity, A is the surface area per unit volume, z is the naphthalene packed-bed length, and $\Delta C_{LM}$ is the log-mean concentration difference across the column defined as

$$\Delta C_{LM} = \frac{\left(C_1^{sat} - 0\right) - \left(C_1^{sat} - C_1\right)}{\ell n \dfrac{C_1^{sat} - 0}{C_1^{sat} - C_1}} \tag{2}$$

where $C_1^{sat}$ is the naphthalene concentration at saturation (*i.e.,* the solubility). Thus $\Delta C_{LM}$ represents the effective driving force for the extration. All of these quantities can be determined from measured experimental quantities except for the surface-to-volume ratio A (which is given to the students) and $C_1^{sat}$, which the students are asked to estimate from an equation of state such as Peng-Robinson (discussion topic #5). The subject of high-pressure phase behavior, including topics such as equilibrium between a solid and a supercritical fluid phase, is covered in the undergraduate thermodynamics sequence at New Jersey Institute of Technology. The pertinent equation is

$$C_1^{sat} = \frac{M_1}{V} y_1 = \frac{M_1}{V} \frac{P_1^{sat}}{P} \exp\left[\frac{V_1^{sol}\left(P - P_1^{sat}\right)}{RT}\right] \frac{1}{\hat{\phi}_1} \tag{3}$$

where $P_1^{sat}$ is the vapor pressure of the solid phase at the system temperature, $V_1^{sol}$ is its molar volume, $M_1$ is its molecular weight, $y_1$ is its mole fraction in the supercritical fluid mixture at saturation, V is the molar volume of the supercritical fluid mixture, and $\hat{\phi}_1$ is the solute fugacity coefficient in the supercritical fluid mixture. Each of the latter two quantities are determined by the chosen equation of state. The equation must be solved iteratively for $y_1$ since the fugacity coefficient is a function of composition. Alternatively, the students could obtain a value for $C_1^{sat}$ from the literature for this quantity.

The value of A, the surface-to-volume ratio for the packed bed, has been experimentally estimated using the student equipment and is given to them. This value is only an order-of-magnitude estimate as it will change each time the column is repacked with fresh naphthalene. This is because the naphthalene crystals are not very uniform in size or shape. This estimate could be improved by adding a size reduction/classification step to the naphthalene to make it more uniform in terms of size and shape. This operation would not necessarily be part of the student experiment, but rather an operation a teaching assistant would perform to ensure that the naphthalene was uniform.

During the experiment the students should have evaluated the mass transfer coefficient k at several different sets of operating conditions. This should allow them to correlate k with key operating conditions. A typical correlation for SCF applications might have a form such as[7,8]

$$N_{Sh} = f\left(N_{Re}, N_{Sc}, N_{Gr}\right) \tag{4}$$

where $N_{SH}$ is the Sherwood number ($kz/D_{AB}$), $N_{Re}$ is the Reynolds number $\left(DV^0\rho/\mu\right)$, $N_{Sc}$ is the Schmidt number $\left(\mu/D_{AB}\rho\right)$, and $N_{Gr}$ is the Grashof number $\left(d^3 g\rho\Delta\rho/\mu^2\right)$. Here, $D_{AB}$ is the diffusivity, D is the column diameter, ρ is the fluid density, Δρ is the density difference between the saturated interface and the bulk, unsaturated fluid, μ is the fluid viscosity, and d is the average particle diameter. The Grashof number, not generally needed in sub-critical fluid applications, is included to account for buoyancy effects. These arise due to the relatively high density and low viscosity and thus exceptionally low kinematic viscosities of supercritical fluids.

The students are thus expected to evaluate the constants in an expression such as

$$\frac{k}{V^0} = a\left(N_{Re}\right)^b \left(N_{Sc}\right)^c \left(N_{Gr}\right)^d \tag{5}$$

Obtaining sufficient data to evaluate all four constants should be one of the objectives when the students develop their experimental plan. In preparing for the experiment, they are expected to have consulted the provided references[9,10] for determining quantities such as viscosity and diffusivity.

In their write-up, the students are expected to address each of the discussion topics listed in Table 1. The first three topics relate to the experimental determination of k, as already described. The remaining topics require that the students comprehend various thermodynamic aspects of SCFE. These include fugacities of solids at high pressures, use of equations of state for high-pressure phase equilibrium, and the Joule-Thomson effect.

## CLOSING REMARKS

Student response to this experiment has been generally positive. They enjoy the "hands-on" experience associated with assembling and disassembling the apparatus, the exposure to a non-traditional unit operation, and the combination of mass transfer and high-pressure thermodynamics in a practical application.

The principal experimental difficulty has been deposition of naphthalene in the discharge line and in the micro-metering valve. This can be alleviated by ensuring that the exiting stream is well removed from saturation. With proper choice of operating conditions, however, the experiment works well as designed. Students can complete several individual experiments in the allotted time of two five-hour laboratory periods.

An alternative experimental set-up would be to replace the discharge line and condensate receiver with a "U-tube" in a cold trap. While this idea is yet to be attempted experimentally, one can envision weighing the tubing (including the

"U-tube") downstream of the micro-metering valve before and after each trial as an alternative to obtaining the amount of naphthalene extracted in the experiment. The mass of the extracted naphthalene would be a more significant portion of the total mass of the sample and apparatus being weighed. In this manner, more accurate results may be possible.

If multiple groups complete the lab during the semester, another enhancement to the laboratory experience could be to have the different groups use different solute materials. At the end of the semester, a comparison of the correlation constants from each group could be completed and this could be used to create a generalized correlation. Possible alternative solutes include biphenyl and benzoic acid. Should this approach be taken, it is important to remember that the value of A, the surface-to-volume ratio in Eq. (1), must be provided for each system investigated.

In summary, this laboratory experiment provides a valuable introduction to a modern unit operation in the chemical process industry while at the same time it encourages creative thinking in the synthesis of concepts from disparate areas of chemical engineering.

## NOMENCLATURE

| | |
|---|---|
| A | Surface area per unit volume of a packed bed ($m^2/m^3$) |
| a,b,c,d | Correlating equation parameters |
| $C_1$ | Average concentration of naphthalene in exiting carbon dioxide ($kg/m^3$) |
| $C_1^{sat}$ | Concentration of naphthalene in carbon dioxide at saturation ($kg/m^3$) |
| $\Delta C_{LM}$ | Log mean concentration driving force ($kg/m^3$) |
| D | Column diameter (m) |
| $D_{AB}$ | Diffusivity ($m^2$/sec) |
| d | Particle diameter (m) |
| g | Acceleration due to gravity (m/$sec^2$) |
| k | Mass transfer coefficient (m/sec) |
| P | Pressure (bar) |
| $P^{sat}$ | Vapor pressure of solute (bar) |
| R | Ideal gas constant ($m^3$bar/molK) |
| T | Temperature (K) |
| V | Molar volume of fluid phase ($m^3$/mol) |
| $V^{sol}$ | Molar volume of solute ($m^3$/mol) |
| $V^0$ | Empty column superficial velocity (m/sec) |
| z | Packed bed length (m) |
| $\rho$ | Density ($kg/m^3$) |
| $\mu$ | Viscosity (kg/m sec) |

*Dimensionless Numbers*

| | |
|---|---|
| $N_{Gr}$ | Grashof number $\left(d^3 g \rho \Delta\rho / \mu^2\right)$ |
| $N_{Re}$ | Reynolds number $\left(DV^0 \rho / \mu\right)$ |
| $N_{Sc}$ | Schmidt number $\left(\mu / D_{AB}\rho\right)$ |
| $N_{Sh}$ | Sherwood number $\left(kz / D_{AB}\right)$ |

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## *Multimedia Fluid Mechanics*

*Continued from page 95.*

The CD is neither a book nor a collection of movie clips. It is truly a seamlessly integrated multi-media tool. The user can read some brief text describing the phenomenon, can look at the equations and see the meaning of each term, and also look at some movie clips that will drive the point home. Most importantly, there are a number of very simple, but cleverly designed, interactive experiments where the user can take data off of a running movie clip and process the automatically tabulated data in order to investigate the dimensional relationships and gain valuable insights. These interactive experiments constitute very nice classroom demonstrations to supplement lectures. An equation feature that is used cleverly is a roll-over feature where as the mouse pointer is dragged over each term of the equation, the term is magnified and highlighted, and its meaning pops up in a small text box.

I cannot overemphasize how well this CD is done. The selection of the topics, the level of coverage, and the actual presentation are all superb. There are many hyperlinks throughout the CD; however, unlike some other CDs where the user can hyperlink his/her way into a digital purgatory, on this CD one can always return to the page of interest using the small navigation map at the top of the page.

Congratulations to Professor Homsy and his colleagues for undertaking the much-needed task of creating a new tool for aiding students of fluid mechanics. Also, congratulations for holding the line on the price, which is extremely reasonable in an environment of skyrocketing textbook prices. ❒