Supercritical fluid extraction of organics from coal gasification wastewaters using carbon dioxide
by Ambrey Gordon Gartner

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

Abstract:
Existing chemical extraction techniques for the removal of phenols from coal gasification wastewater require a moderately expensive solvent and additional distillation equipment for solvent recovery. This research was designed to determine if supercritical carbon dioxide, a non-toxic, non-flammable, and relatively inexpensive byproduct of coal gasification, could be used for phenol extraction.

Experiments were run to investigate phase equilibria associated with the two phase system consisting of water, phenol, and carbon dioxide. System pressures varied between 1100 and 3000 psi at a temperature of 40 degrees Celsius. Phenol concentrations in the water phase varied from 600 to 8500 mg/l. Phase equilibrium data were first used to determine the ability of supercritical carbon dioxide to extract phenol from water, and later to determine the extraction column characteristics.

Extraction equipment was built to test the feasibility of continuous extraction of phenol from water and wastewater. Twenty-three successful experiments were run, including one counter-current and seventeen co-current experiments using phenol/water standards of known initial concentration, and five co-current experiments using wastewater. The best extraction capability was obtained using counter-current extraction techniques.

Extraction efficiencies, based on the approach to theoretical equilibrium, were determined for each of the co-current experiments. These efficiencies ranged from 81% to 145% for the phenol/water standard experiments, and from 76% to 163% for wastewater experiments. Relative extraction efficiencies were based on Run No. 5, which had the highest efficiency of a phenol/water standard experiment (145%). Extraction of phenol and phenol derivatives from coal gasification wastewater appeared to be higher than would be expected, based on equilibrium data. This could be due to additional experimental error involved in measuring the original phenol concentration in the wastewater. Also, the existence of co-solvents in the wastewater could enhance the solvent power of supercritical carbon dioxide.

SUPERCRITICAL FLUID EXTRACTION OF ORGANICS FROM COAL GASIFICATION WASTEWATERS USING CARBON DIOXIDE

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APPROVAL

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Ambrey Gordon Gartner

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the college of Graduate Studies.

10/23/85
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Nov. 7, 1985
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ABSTRACT

Existing chemical extraction techniques for the removal of phenols from coal gasification wastewater require a moderately expensive solvent and additional distillation equipment for solvent recovery. This research was designed to determine if supercritical carbon dioxide, a non-toxic, non-flammable, and relatively inexpensive byproduct of coal gasification, could be used for phenol extraction.

Experiments were run to investigate phase equilibria associated with the two phase system consisting of water, phenol, and carbon dioxide. System pressures varied between 1100 and 3000 psi at a temperature of 40 degrees Celsius. Phenol concentrations in the water phase varied from 600 to 8500 mg/l. Phase equilibrium data were first used to determine the ability of supercritical carbon dioxide to extract phenol from water, and later to determine the extraction column characteristics.

Extraction equipment was built to test the feasibility of continuous extraction of phenol from water and wastewater. Twenty-three successful experiments were run, including one counter-current and seventeen co-current experiments using phenol/water standards of known initial concentration, and five co-current experiments using wastewater. The best extraction capability was obtained using counter-current extraction techniques.

Extraction efficiencies, based on the approach to theoretical equilibrium, were determined for each of the co-current experiments. These efficiencies ranged from 81% to 145% for the phenol/water standard experiments, and from 76% to 163% for wastewater experiments. Relative extraction efficiencies were based on Run No. 5, which had the highest efficiency of a phenol/water standard experiment (145%). Extraction of phenol and phenol derivatives from coal gasification wastewater appeared to be higher than would be expected, based on equilibrium data. This could be due to additional experimental error involved in measuring the original phenol concentration in the wastewater. Also, the existence of co-solvents in the wastewater could enhance the solvent power of supercritical carbon dioxide.

INTRODUCTION AND PREVIOUS RESEARCH

Introduction

One of the major engineering challenges of this century will be the conversion from an energy system based on naturally occuring crude oil to a system based on the production of synthetic fuels. Future fuels will consist of hydrocarbons, alcohols, and hydrogen produced mainly from coal, but also from lignite, peat, biomass, and eventually from genetically programmed organisms utilizing sunlight.

In the production of synthetic fuels from coal and lignite, one of the main goals of most existing technology is the production of carbon monoxide and hydrogen, commonly called synthesis gas. These chemical building blocks are then combined in a variety of ways to form a wide spectrum of hydrocarbons and alcohols. However, in the production of the synthesis gas, there are many side reactions involving steam, elemental carbon, and the complex mixture of molecules that comprise coal and lignite. Given the appropriate reactor residence times, temperatures, and pressures, a family of prominent side reactions are associated with any particular type of conversion facility.

The Lurgi coal gasification reactor, one of the older and more proven technologies, produces a significant amount of water soluble chemicals, including phenols, phenol derivatives, and ammonia. Data obtained from the Grand Forks Slagging Gasifier at the Grand Forks Energy Research Center indicate that this type of reactor typically produces wastewater streams containing up to 8000 parts per million (ppm) phenol and phenol derivatives, and ammonia concentrations approaching 14,000 ppm. As a result considerable effort and expense are required to remove these components from process water. These concentrations are toxic to micro-organisms commonly used in wastewater treatment, resulting in designs relying on chemical treatment. Standard liquid-liquid extraction of phenols from water with isopropyl ether requires a moderately expensive solvent and the addition of extra distillation equipment for solvent recovery.

There are distinct advantages for finding another solvent that would eliminate the need for the additional separations equipment. Carbon dioxide appears to be an economically attractive solvent because it is a readily available coal conversion byproduct and could be used on a once-through basis without recovery. Fortunately, carbon dioxide is also an effective solvent for supercritical fluid extraction (SCFE) and has been used to remove organics from many solid mixtures. Applications of SCFE using carbon dioxide include isolating valuable constituents from natural materials like oil seeds, hops, and spices and removing or reducing levels of undesirable substances such as nicotine or caffeine. However, there are few, if any, commercial applications where supercritical carbon dioxide is used to extract components from a liquid.

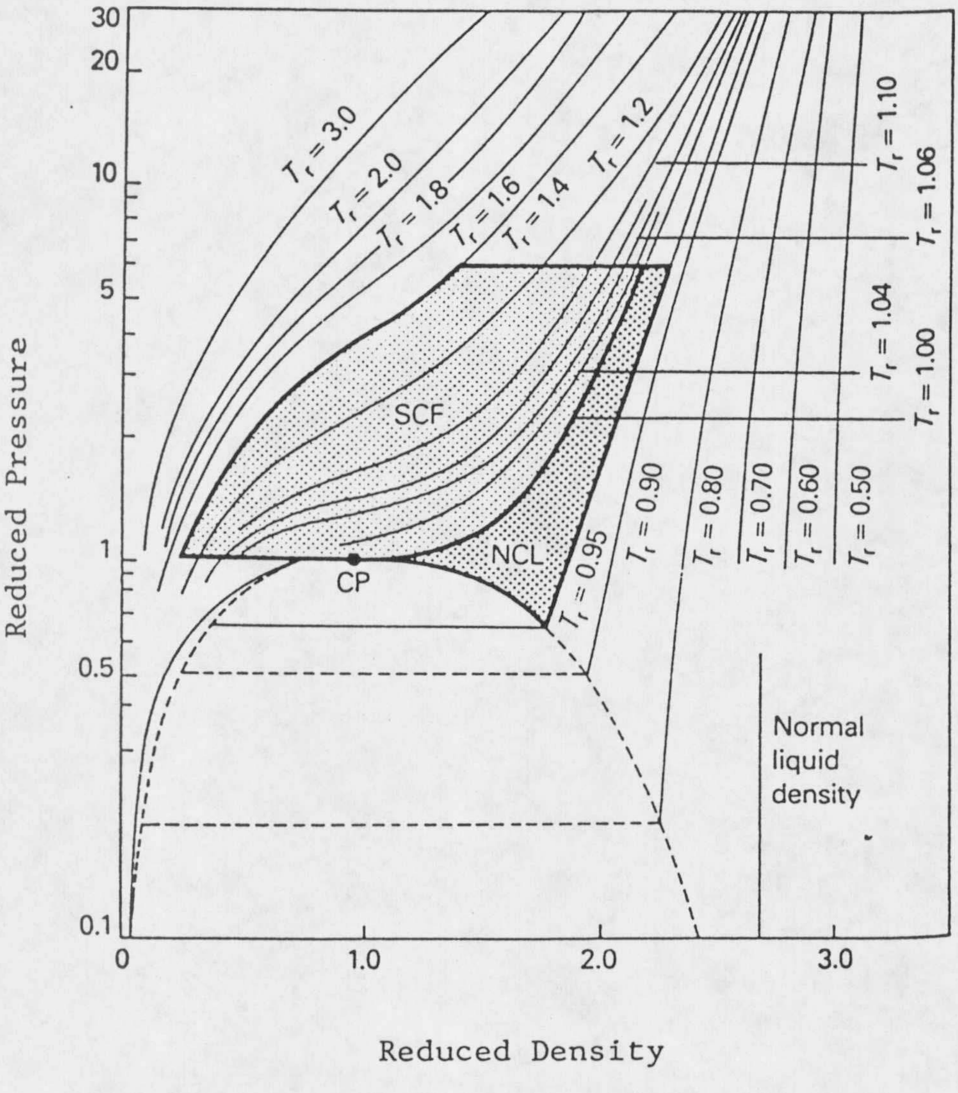
Supercritical Fluids

All substances possess a critical temperature, above which the liquid phase cannot exist. At the critical temperature the pressure that must be applied to cause condensation is called the critical pressure. Alternatively, the critical pressure can be regarded as the vapor pressure of the liquid at its critical temperature (1).

When a liquid is heated in a sealed container, the properties of the liquid and vapor approach one another near the critical temperature. Below the critical temperature there are two distinct phases. As the sample is heated through the critical temperature, the meniscus separating the two phases disappears and one phase results. This phase is referred to as a supercritical fluid. Although the fluid has properties of both a liquid and a gas it is in reality neither a gas nor a liquid.

At supercritical temperatures a substance that is gaseous at ambient conditions will begin to behave like a liquid when the pressure is raised sufficiently. Below $31^{o}C$, for example, liquid carbon dioxide can be used to dissolve natural oils and a wide range of other animal and vegetable materials. At temperatures greater than $31^{o}C$ carbon dioxide does not liquify, but it still can be used as a solvent if the pressure is raised sufficiently for its density to become similar to that of a liquid (2).

The supercritical fluid (SCF) region for a pure component is generally defined as that region of temperatures and pressures greater than or equal to the critical temperature and critical pressure of the pure component. For practical considerations, the SCF region of interest is defined less rigorously here to include the conditions bounded approximately by $0.9 < T_r < 1.2$ and $P_r > 1.0$. In this region the SCF is highly compressible, as illustrated by de Filippi (3) in Figure 1. For example, at a constant T_r of 1.10, increasing pressure from $P_r < 1.0$ to $P_r > 1.0$ significantly increases the density from relatively low values to liquid-like densities. At higher reduced temperatures, the pressure increase required to produce an equivalent density increase becomes greater. This practical consideration sets the upper bound on temperature. At a constant P_r of 1.50,



Taken from de Philippi (3).

Figure 1. Reduced Pressure-Density Diagram Showing Supercritical Fluid (SCF) and Near Critical Liquid (NCL) Regions.

decreasing temperature has a similar effect on density, and at higher reduced pressures, the density is less sensitive to temperature changes. In the vicinity of the critical point, large density changes can be produced with either relatively small pressure or temperature changes (4).

The use of supercritical fluids as solvents for extraction has unique advantages. Supercritical fluids combine the solvent power of a liquid with the transport properties of a gas. They can be used to selectively dissolve relatively involatile solutes from a mixture while allowing the simple separation of solvent and solute by either a reduction in pressure or an increase in temperature. Pressure is the principal processing variable used to alter the solvent power. In contrast, liquid extraction solvent power is varied by adjusting the temperature or the solvent composition; allowable temperatures are limited by the thermal characteristics of the solute while variations in solvent composition increase separation and purification costs. Significant reductions in energy requirements are also characteristics of SCFE separations (5).

Extraction with Supercritical Fluids

Supercritical fluid extraction (SCFE) is a technique that exploits the solvent power of supercritical fluids at temperatures and pressures near the critical point. By selectively choosing the appropriate solvent a wide range of operating temperatures and pressures can be utilized to tailor an extraction process design to a particular need.

It is possible to dissolve both solids and liquids (including ones of low volatility) in compressed gas. The behavior of gas/solid systems is normally simpler than that of gas/liquid systems as the composition of the solid phase normally remains constant. When a liquid is being extracted, the situation is complicated by the influence of dissolved gas on the properties of the liquid phase (2).

The advantages of using supercritical fluids under pressure include the following:

> High boiling components can be extracted at relatively low temperatures. Also, at the lower temperatures involved, heat sensitive compounds are undamaged during the extraction process.

> Separation of the solute and solvent is relatively easy at supercritical conditions, usually by relatively slight pressure changes.

> Separations can be achieved which are not possible by other techniques such as distillation or extraction.

If food components are to be separated, non-toxic solvents, such as carbon dioxide, may be used which leave no harmful residues.

In general terms, compressed gases are relatively cheap solvents.

The difficulties which have to be overcome include the following:

High plant costs involving relatively high risk capital.

Cost of maintenance normally required for high pressure plants.

Current lack of process design data and lack of information on equipment reliability.

In many unique and difficult processes there is a tendency to use patent laws as a protection against competition. The mass of patents in the field makes it extremely difficult to determine if infringement is likely in a particular application.

Supercritical fluid extraction is particularly effective in the isolation of substances of medium molecular weight and relatively low polarity. Its principal advantage over distillation is that separation can be accomplished at moderate temperatures, and thus can be applied to the recovery of heat-labile substances of low volatility. It is therefore of interest in the food and petroleum industries.

In comparison with liquid solvents, the supercritical fluid has high diffusivity and low density and viscosity, allowing rapid extraction and phase separation. The solvent power of the supercritical fluid can be varied over a wide range by varying pressure or temperature, and the fluid is easily recovered from the extract and from the extraction residue as a result of its high volatility. Again, the principal disadvantage of SCFE is the relatively high pressures required to achieve the necessary densities, generally in the range of 50 to 200 atmospheres. Another disadvantage is the complexity of the phase relationships under supercritical conditions. Theoretical techniques for predicting extraction behavior are new and relatively untested. An extensive bibliography assembled by McKugh and Krukonis (6) shows that most of the modeling work in this area has been developed in the last ten years (7 - 19).

The SCFE concept was first recognized by Hannay and Hogarth (20) over a hundred years ago. They observed that potassium iodide was dissolved in supercritical ethanol and was precipitated on reducing the pressure. Later it was realized that the solvent power of supercritical fluids could be involved in geological processes through the influence of water on rock formation, and of methane in petroleum formation and migration. In power stations the adoption of supercritical steam pressures led to the deposition of silica on the blades of steam turbines (21).

The possibilities for substantial energy economies, relative to normal distillation processes, have made SCFE an area of intense interest. Arthur D. Little (5) probably triggered this interest with the claim that supercritical fluid extraction would make it possible to produce a gallon of ethanol using carbon dioxide as extractant with an expenditure of 10,000 Btu of energy instead of the 25,000 to 50,000 Btu needed for conventional distillation.

Carbon Dioxide as a Solvent

Carbon dioxide has many characteristics which make it suitable for use as a solvent. It is completely miscible with low molecular weight hydrocarbons and oxygenated organics and is therefore a good solvent for many organics (3,22). It is relatively volatile, compared with most organics likely to be extracted, allowing easy separation. In addition, carbon dioxide has low viscosity and high diffusivity, and it is totally non-toxic, non-flammable, and relatively inexpensive (23).

The solubility of supercritical carbon dioxide in water is relatively small, generally less than seven weight percent, even at pressures exceeding 400 atmospheres. At near critical conditions, for example at 40°C and 80 atmospheres, the solubity is approximately 5.5 weight percent (24). This allows the use of carbon dioxide for a variety of extraction chores involving aqueous solutions. Furthermore, carbon dioxide can be removed easily by simple deaeration techniques.

As a supercritical fluid carbon dioxide has additional properties that make it an excellent solvent. Its critical temperature (31^{o}C) and pressure (72.8 atm) are readily accessible with well-established process technology and equipment. Finally, its heat of vaporization is low, especially near the critical point, leading to low energy requirements in many processes (3).

Table 1 shows a comparison of the fluid properties of carbon dioxide as a liquid, a supercritical fluid, and as a gas (3, 24). The ranges shown for the supercritical fluid are those in the near critical region. At sufficiently high pressures (approximately 500 atm at 40^{o}C) the density of supercritical carbon dioxide can actually exceed 1 g/cc. Also, in the near critical region significant energy savings can result due to the very low heats of vaporization. Table 2 shows selected data relating temperature, pressure and heat of vaporization (3). The zero value listed at the critical point illustrates the unique quality that any fluid possesses when the distinction between a liquid and a gaseous phase disappears.

Table 1. Comparison of Carbon Dioxide Fluid Properties.

	Liquid	Supercritical	Gas
Density (g/cc)	0.5 - 1.2	0.2 - 0.7	0.001
Viscosity (cP)	0.5 - 1.0	0.05 - 0.10	0.01
Diffusivity (cm^2/s)	10^{-5}	10^{-4} - 10^{-3}	10^{-1}

Table 2. Heat of Vaporization of Carbon Dioxide.

Temperature °F	Temperature °C	Saturation Pressure (atm)	Heat of Vaporization (Btu/lb)
0	-17.8	20.8	120.1
20	4.4	38.6	95.0
60	15.6	50.9	76.6
70	21.1	58.1	63.8
80	26.7	65.9	44.8
87.8	31.0	72.7	0

Supercritical fluid extraction with carbon dioxide has been used extensively in the food industry. Here the properties of being non-toxic and non-flammable have significant advantages when extracting such valuable products as perfume oils, caffeine, hops, and vegetable oils. It also is possible to remove PCB's from silicon-based transformer oils and to remove adsorbed materials from common adsorbents such as activated carbon and synthetic resins. Table 3 shows a number of examples of the use of carbon dioxide for supercritical fluid extraction.

Table 3. References with Examples of Supercritical Fluid Extraction Using Carbon Dioxide.

Substance	T, ^{o}C	P, atm	ref.
Vegetable oil	20, 55	150-450	3
Polychlorinated biphenyls (PCB)	100	120-265	3
Silicone oil	100	160-250	3
Alachlor (pesticide)	50 - 120	88-272	3
Caffeine	90	160-220	21
Hops	< 40	unidentified	25
Lilac oil	34	90	26
Lemon peel	40	300	27
Black pepper	60	100-400	27
Almond oil	40	600	27

Previous Research

Research done previously at Montana State University has investigated the use of supercritical fluids for separating organics from the undesirable mineral portion of peat. Granlund (28) and Smith (29) investigated the semi-continuous flow extraction process where a variety of supercritical and near supercritical fluids were passed through a container containing a measured amount of peat. Organics were extracted from the mineral portion of the peat and yields were measured for each type of solvent used. Earlier work performed by Myklebust (30) investigated the potential for utilizing supercritical fluids for batch extraction of organics from peat.

The University of Delaware Chemical Engineering Department has been active in SCFE research. Van Leer and Paulaitis investigated the solubilities of phenol and chlorinated phenols in supercritical carbon dioxide (31), and McHugh and Paulaitis investigated the solubilities of solid naphthalene and biphenyl in supercritical carbon dioxide (32).

Kurnik, Holla, and Reid (33) of the Massachusetts Institute of Technology studied the solubility of several solids in supercritical carbon dioxide and ethylene. They include a table of references with the solubilities of various solids in supercritical fluids. This data is shown in Table 4.

Table 4. References with Solubility of Solids and Liquids in Supercritical Carbon Dioxide.

Substance	T, C	P, atm	ref.
Naphthalene	35, 45, 55	100-300	23
Naphthalene	35-55	60-330	34
Ethanol/Water	40, 60	75-204	35
Isopropanol/Water	40	102	35
Phenanthrene	40	135-544	36
Diphenylamine	32-37	50-225	37
Phenol	36, 60	78-239	31
Chlorinated Phenols	36	80-130	31
Napthalene	35-65	86-288	32
Biphenyl	36-58	105-484	32
Biphenyl	55	503-531	38
Naphthalene	58-80	1-250	38

Probably the most extensive research involving the solubility of various substances in carbon dioxide was published by Francis in 1954 (39). Mutual solubilities of liquid carbon dioxide with each of 261 other substances were reported. Nearly half of these substances are miscible with carbon dioxide. Francis noted some relations to structure and plotted phase diagrams for 464 ternary systems involving carbon dioxide. He also pointed out that carbon dioxide has a strong homogenizing action upon pairs of other liquids at moderate concentrations, but a precipitating action at higher concentrations. In contrast to most solvents it has a selectivity against dicyclic hydrocarbons. Co-solvents were found necessary to make these unusual properties effective in the solvent extraction of hydrocarbon mixtures. While this paper does not include any research involving a supercritical phase, the measurement conditions ("liquid carbon dioxide at or near room temperature") are in the near-critical region, and the data provides an invaluable tool for roughly estimating the probable success one might have using supercritical carbon dioxide with any of the same combinations of substances. Using some of the groupings that Francis presents might also help predict the suitability of using supercritical carbon dioxide as an extractive agent for similar mixtures.

RESEARCH OBJECTIVE

The purpose of this research is to investigate the feasibility of using supercritical carbon dioxide to extract phenols from coal gasification wastewater. In order to achieve this ultimate objective the work presented in this paper focuses on the development and testing of the necessary extraction equipment, investigation of water/phenol/carbon dioxide equilibrium data, and the development of procedures for analyzing phenols in dilute aqueous solutions.

Extraction equipment was ordered, assembled, tested, and modified to obtain phenol extraction data at approximately 40°C and pressures ranging from 1100 to 2800 psig. Efforts were made to obtain data representing continuous flow conditions, both counter-current and co-current. These data are compared with the equilibrium data, obtained as part of this research, to evaluate the effectiveness of each set of extraction conditions.

MATERIALS, EQUIPMENT, AND PROCEDURE

Materials

Carbon dioxide was obtained as a technical grade liquid, heated, and compressed into a special bottle rated at 6000 psi. A Haskel Model AGD-62-C Gas Booster compressor was used to boost the CO_2 from approximately 850 psi to 5000 psi.

Original extraction data was obtained using a 10,000 mg/l reagent grade phenol in distilled water standard solution. After the extraction equipment had been sufficiently tested and operating parameters better understood, another type of solution was tested for extraction. This solution was obtained from the Grand Forks Energy Research Facility and consisted of process water condensed from their experimental slagging gasifier.

Equipment

Equilibrium Data Equipment

Equipment used for generating phase equilibrium data included a Parr Instrument Company Series 4000 pressure reaction apparatus. This 500 milliliter bomb was constructed of Inconel 757-S alloy. The bomb was specially fitted with a modified head to allow two valves for filling with the appropriate phenol/water solution and pressurizing with carbon dioxide. One of the valves was also used for sampling the liquid phase. The apparatus also included a rocker equipped with an electrical heater which was used to keep the fluids thoroughly mixed at 40^{o}C. The bomb temperature was monitored using a thermocouple located at the base of the bomb and connected to a 12 channel temperature indicator. Temperature was manually controlled by a Fisher Scientific rheostat which supplied power to the rocker heating coils.

Extraction Apparatus

The equipment used in this research was designed to facilitate extracting phenol from water on a continuous basis. Figure 2 shows a schematic of the original extraction equipment. The carbon dioxide and water feed systems were essentially unchanged for the duration of all the extraction runs. All of the significant equipment changes involved the column itself and solution and solvent discharge lines. Essentially all the high pressure lines used in this research were located behind a three-sided,

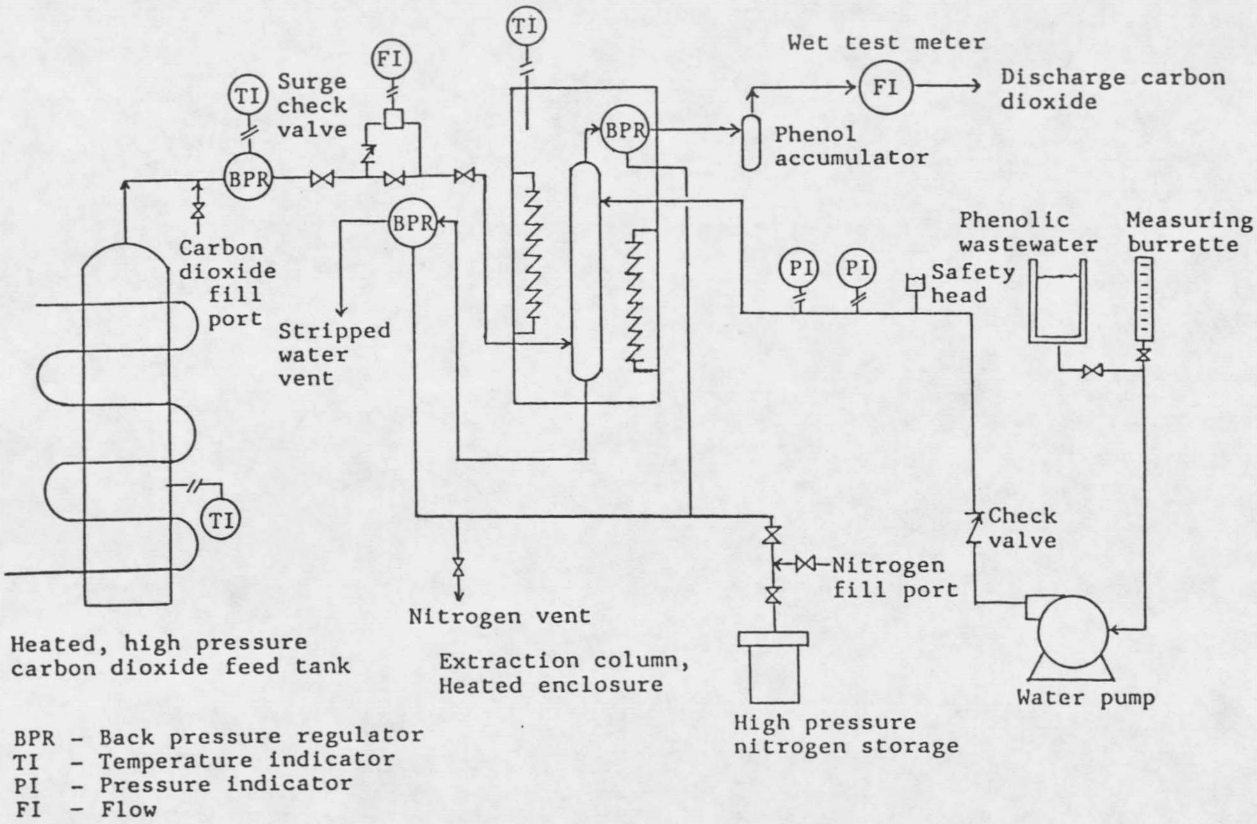


Figure 2. Schematic of Counter-current Extraction Apparatus as Originally Designed and Built.

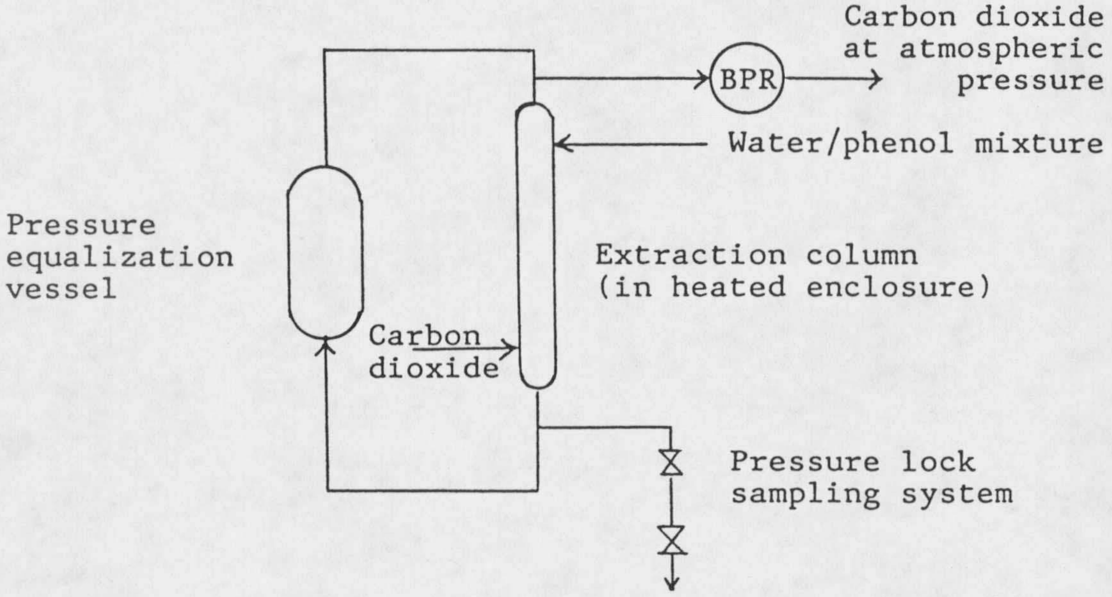
high-strength steel shield. Control valves, gages, and electronic meters were accessible from the front of the shield.

Carbon dioxide was stored under sufficient pressure to provide the appropriate test pressure for each run. The Haskel Gas Booster compressor was used to transfer CO_2 from a standard cylinder to a special high pressure cylinder rated at 6000 psi. The high pressure cylinder was warmed to supercritical temperatures (approximately 40°C) using an electrical heating blanket. The temperature was manually controlled with a Powerstat Type 3PN1168 variable transformer, and monitored using a thermocouple connected to a Cole-Palmer Model 8530 12 channel electronic indicator. Carbon dioxide pressure was regulated by a Tescom Model 44-1126-24-013 back pressure regulator. Heat was supplied with a 100 watt electrical heat tape as the pressure was reduced to provide heat of vaporization and to further raise the temperature to approximately 40°C. The temperature was measured with a thermocouple attached to the regulator surface and monitored using the Cole-Palmer indicator. From the regulator the solvent then entered a system of control and check valves which provided flow control to the extraction column. Once the carbon dioxide had passed through the column its pressure was reduced to atmospheric using a

Grove Mity-Mite Model S-91XW back pressure regulator. Back pressure was supplied by a Parr Instrument Company Series 4000 pressure reaction apparatus filled with nitrogen up to 5000 psi. This 500 milliliter bomb was constructed of Inconel 757-S alloy. Once again the solvent stream was heated with electrical heat tape (200 watts) while its pressure was reduced. This was to prevent icing (both water and CO_2) and to help prevent the deposition of solid phenol in the regulator and exiting tubing. Both heat tapes were manually controlled with a Powerstat Type 3PN1168 variable transformer. Atmospheric carbon dioxide was then passed through a Parkinson Cowan wet test meter to measure the actual solvent flow rate. The CO_2 ports were designated as inlet/outlet ports since they were used as such depending upon whether the particular extraction was counter-current or co-current.

The phenol/water solution was stored in a stainless steel Griffin beaker. Solution was gravity fed from the beaker into a Milton Roy Model HDB-1-30R pump capable of delivering a maximum of two milliliters per minute at 3000 psi. The flow rate was measured by timing the removal of solution from a burette and valve apparatus as shown in Figure 2. The solution was then pumped through 1/4 inch stainless steel tubing past a check valve, a rupture disc, two pressure indicators, and into the extraction column. The pressure was measured by a Model DPS 0081 electronic pressure sensor made by Autoclave Engineers and by a 5000 psi gage used as a cross-check. After pressure measurement the solution lines entered an oven containing the extraction column. The 1/4 inch lines were then reduced to 1/8 inch before actually entering the column through a side port located near the top of the cylindrical portion of the column. The water entry port was located approximately one inch below the CO_2 inlet/outlet port.

Water and CO_2 exiting the column were originally reduced to atmospheric pressure using the same type of back pressure regulator. Both back pressure regulators were connected to the same nitrogen pressure system, as shown in Figure 2, so that the entire column and the fluids flowing through it would sense the same conditions. However, the slight differences in the regulators were enough to prohibit the use of this arrangement. The column length between the water inlet and the water outlet, determined by the regulator position, was limited to approximately 20 inches, or a pressure head of less than one psi. At system pressures between 1100 and 3000 psi the back pressure regulators just could not provide the necessary control. The extraction equipment was then modified, as shown in Figure 3, so that water exiting the column would enter the bottom of a bomb that was pressurized by a "vapor" line

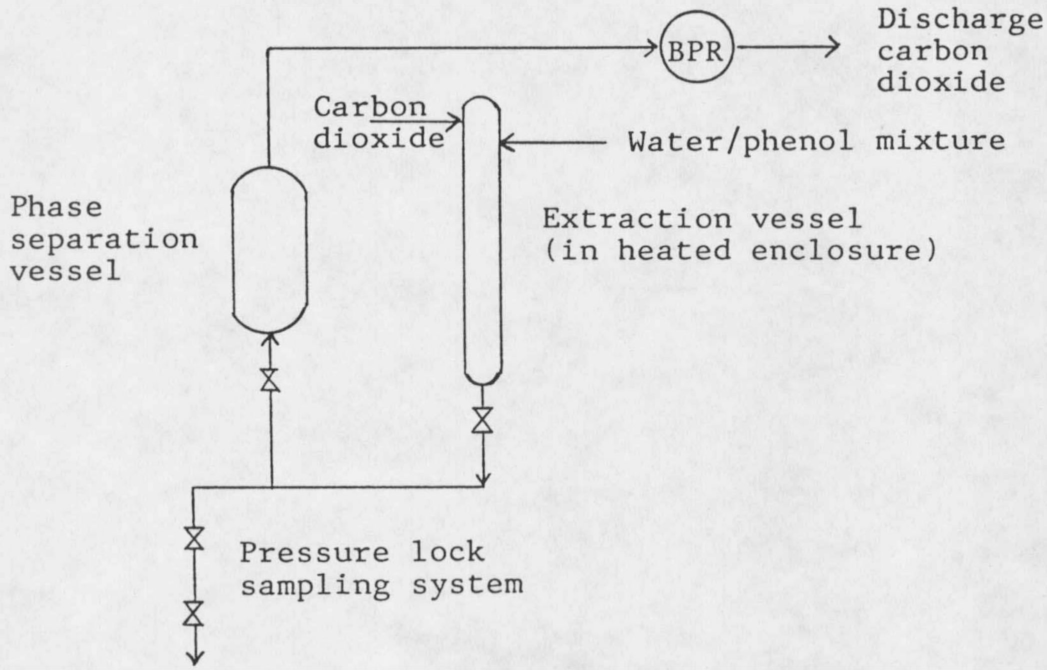


BPR - Back pressure regulator

Figure 3. Schematic of Workable Counter-current Extraction Apparatus.

from the top of the column. Extracted water accumulated in the bomb until the run was considered complete. A pressure lock system of valves allowed the removal of approximately four milliliters of extracted water for sampling purposes.

A final major equipment modification was made to enable co-current extraction runs. A schematic of this arrangement is shown in Figure 4. Here, the pressure equalization vessel doubles as a phase separator and vessel to store



BPR - Back pressure regulator

Figure 4. Schematic of Co-current Extraction Equipment.

extracted solution until the end of the run. Valves at the bottoms of the settler vessel and extraction column were added to enable each system to be isolated while lines were being purged and sampled.

The extraction column itself was totally enclosed in a steel box which was fitted with two 500 watt electrical heaters manually controlled by a Powerstat Type 3PN1168 variable transformer. Oven temperature was measured by a thermocouple and monitored by the Cole-Palmer indicator. The column was 12 inches long with an inside diameter of 0.688 inches and outside diameter of one inch. The top end of the column was fitted with a custom-machined steel fitting having three ports, The top fitting had three ports, a carbon dioxide inlet/outlet port, a water solution inlet port, and an unused port. The bottom of the column was fitted with an Autoclave Engineers tee having two ports, one for the carbon dioxide inlet/outlet port, and the other for the water outlet. All four inlet and outlet ports were reduced to 1/4 inch NPT openings. Three of these openings were reduced further to 1/8 inch Swagelok fittings to facilitate tubing connections in the close quarters available in the oven. The fourth opening, located at the lowest point, was used for the extracted water solution outlet. This port provided a straight line path for the exiting water solution and was left as large as possible to reduce any flow restrictions.

Three types of column packing were used in separate trials. These included 1/4 inch glass Raschig rings, 1/16 inch glass helices, and 1/16 inch steel helices. Support screens were cut to fit the column ends to prevent packing from entering any of the inlet/outlet ports.

Analytical Equipment

Phenol concentrations were measured using a Varian 1800 Series Gas Chromatograph with a flame ionization detector. A new custom packed glass column, specifically designed for phenol and phenol derivatives analyses, was obtained and preconditioned according to the manufacturer's specifications. The column packing consisted of KG-02 on Uniport HP, with 80/100 mesh. Column length was ten feet with a two millimeter inner diameter and 0.125 inch outer diameter. All the phenol analyses for this project used this single column at an oven temperature of 175°C, with a helium carrier gas and a hydrogen flame.

While this research did not involve the removal of ammonia or chemical oxygen demand, it was anticipated that future work would. Equipment was therefore organized for the analysis of these two parameters. An Orion 901 Ion-alyzer with an ammonia ion-specific electrode was prepared to measure ammonia concentrations. The complete procedure and specific reagents used in the ammonia analyses are presented in Appendix A. Chemical oxygen demand standards were measured using a large hot plate, a thermometer reading at least 200°C, 500 milliter Erlenmeyer flasks, and reagent grade chemicals including mercuric sulfate, ferroin indicator, ferrous ammonium sulfate, concentrated sulfuric acid, and rapid dichromate acid solution. The special reagents and procedures used in this method are described in Appendix A.

Experimental Procedures

Phase Equilibrium Run Procedures

A known volume, usually 100 milliters, of a phenol/water standard was poured into the Parr bomb. The standard consisted of a known concentration of phenol, either 625, 1250, 2500, 5000, or 10,000 mg/l. Carbon dioxide was then compressed into the bomb to a pressure of about 1000 psi for the low pressure tests and to about 1500 psi for the high pressure tests. The bomb was then placed in the rocker (but not rocked) and heated to 40^{o}C to obtain a pressure reading. Carbon dioxide was added or vented as needed to attain the desired system pressure. The rocker was then set in motion and the heat adjusted so that the system would stay at 40^{o}C for at least 10 minutes. After the system had stabilized the rocker was stopped and the bomb placed in an inverted position while the temperature was maintained. The liquid phase and the supercritical fluid phase were allowed to separate for about five minutes and a small amount of fluid was allowed to be vented. Immediately after the initial venting a three milliliter liquid sample was taken for analysis.

Extraction Run Preparations

In preparation for each run the high pressure carbon dioxide cylinder was checked to see if there was sufficient solvent pressure for the particular run and if the bottle temperature was approximately 40°C. Powerstats were set to approximate settings to maintain the carbon dioxide temperature across both pressure drops and to maintain the oven temperature at 40°C. Experience was the best guide as to what settings would be required. If the high pressure cylinder needed to be recharged the Haskel compressor intake was connected to a liquid CO_2 cylinder at room temperature, the discharge was connected to a port located on the front of the panel, the appropriate valves were opened and closed, and the compressor was started. When the high pressure cylinder was charged to about 4500 psi the valves were reset and the compressor was disconnected.

Also, before a run was begun, the back pressure regulator system was set to the desired system pressure and a check made for an essentially perfect seal. A nitrogen leak during a run of any reasonable length would cause the system pressure to change and ruin an otherwise good run. Once the original equipment was in place the nitrogen system was very reliable. Occasionally the high pressure nitrogen bomb would also need to be recharged due to manual adjustments in the pressure settings. The Haskel compressor intake was then connected to a nitrogen cylinder and the discharge to a special nitrogen port on the front of the panel. Each back pressure regulator was isolated from the bomb, and the bomb was then charged with up to 5000 psi of nitrogen. The compressor was then disconnected and the back pressure regulator system was charged with whatever pressure was desired.

The phenol/water solution was checked before and during each run to ensure that the pump would not run dry and to provide a continuous feed to the column. All but the last five runs were charged using a 10,000 mg/l phenol standard prepared in the lab. The last five runs were charged with actual coal gasification wastewater containing approximately 5000 mg/l phenol, a variety of cresols, ammonia, and other organics.

The wet test meter was checked before each run for the proper water level and proper gas seal. The carbon dioxide discharge line was vented into a 500 milliliter flask to allow any solids or liquids to drop out before entering the wet test meter. The flask was checked for a proper seal.

Extraction Run Procedures

Although there were several different types of equipment arrangements, most of the experimental procedures were essentially the same. The principal differences involved the collection of extracted solution samples. At the start of each run the Tescom back pressure regulator was adjusted to approximately 50 to 100 psi higher than the system pressure. The carbon dioxide feed control valves were then used to fine-tune the solvent flow rate for each particular run. This flow rate was one of the principle changeable parameters for each run and, as it turned out, was one of the biggest sources of problems in producing reliable extraction data. Once solvent flow was reasonably established the water solution pump was started and the flow rate checked and adjusted if necessary. Usually the solvent flow would then need to be readjusted to fine-tune the balance between solution and solvent flow.

After both solvent and solution flows were established at reasonally constant rates the time and the wet test meter reading were recorded. Periodic flow checks were made to ensure that the flows remained constant. Adjustments were made as necessary to keep the system as close to a steady-state as possible. Almost always the only adjustment necessary was the adjustment to the carbon dioxide flow. This was due to the constantly varying pressure on the high pressure side of the Tescom back pressure regulator, which changes the cooling effect across the regulator and the subsequent heat requirement of the manually controlled heat tape. Slight changes in original carbon dioxide pressure required periodic control valve adjustments as the run progressed.

Once the run was considered to have reached steady-state (approximately two to six hours, depending on carbon dioxide mass flow rate) the solvent and solution flows were stopped and the extracted solution was sampled. This allowed a sufficient amount of solution to accumulate in the bottom of the collection bomb to enable a representative sample to be taken. Valves located at the bottom of the column and at the bottom of the collection bomb were closed immediately after the flows were stopped. The system was then allowed to rest, undisturbed, for approximately five minutes to allow any phenol-laden (pregnant) carbon dioxide that was undissolved in the water phase to float to the surface of the water phase. The sample line between the two valves was then drained via the lock valves. The valve below the collection bomb was then reopened to allow the liquid in the bottom of the bomb to flow into the sampling line. Liquid samples were then removed, approximately 3.5 milliliters at a time, and collected in labeled sample vials.

Originally, each vial was analyzed to get some idea of whether the runs were indeed long enough and to check if the concentrations of phenol changed significantly with each sample. It appeared that the first flush, which included both solution and solvent, was not representative. Actually, that result was expected for co-current flow conditions since any phenol dissolved by the carbon dioxide would be redeposited when the combined mixture was reduced to atmospheric conditions. Also, the first sample after reopening the bomb bottom valve was questionable since carbon dioxide may have been trapped in some of the tubing immediately below the bomb. This sample analysis was normally discarded. Once several runs had been analyzed it appeared that the first line flush should be discarded along with at least the first three to four milliters of solution in the bomb. Then, approximately 10 milliters of extracted solution would be collected in a graduated cylinder and about three to four milliters transferred to a labeled vial for later analysis. These samples were considered representative of the steady state conditions during each run.

The last bit of liquid to be sampled from the bomb was generally accompanied by a considerable amount of carbon dioxide and was considered to be non-representative of steady-state conditions. This sample was discarded, and generally the analysis of the one previous sample was considered questionable if it varied significantly from the average of the earlier samples.

Sample Analyses

Phenol concentrations were measured using a Varian 1800 Series Gas Chromatograph (GC) with a flame ionization detector. All the phenol analyses for this project used the packed glass column, specifically designed for phenol and phenol derivatives in a polar solvent (water). The helium flow rates were varied as needed to maintain reasonable peak sharpness, peak separation, and analysis time. Normal helium flow rates corresponded to regulated helium pressures of 25 to 40 psig supplied to the column. Air and hydrogen were adjusted to approximately a 10:1 flow ratio sufficient to maintain a stable flame. The attenuation and range were adjusted to attain a peak height suitable for the particular phenol concentration range in question, ideally a peak height approximately 80% of full scale. A prepared phenol standard was then injected to determine a basis for unknown sample measurement. Typically, a sample size of approximately one microliter was used and enough repetitions were made of standards and samples to account for slight variations in sample sizes.

A concerted effort was made to use the same sample size for both standard and unknowns to eliminate any unnecessary measurement errors due to detector sensitivity, column overloading, or other parameters.

Since even the highest phenol concentrations were only one percent (10,000 mg/l) phenol, very sensitive settings were required. Even so, the peaks were not ideal, often having wide bands with trailing tails. In order to be consistent the areas under the top half of each peak were measured. Unknown sample concentrations were calculated based on a directly proportional comparison of the average area of the standards. For example, an unknown sample peak with an area of 1.2 times the area of the standard's peak would have a concentration 1.2 times that of the standard, assuming the sample sizes were the same and the attenuation, range, and all other parameters were constant. Helium flow rates were kept constant, as much as practical, during any particular analytical run, and only changed to adapt to the measurement of new phenol standards.

A few problems were encountered due to sample sizes. Excessive sample sizes, generally greater than two microliters, sometimes caused wide peaks with excessively large tails, off-scale problems, and carrier gas pressure (flow) swings. Too small sample sizes created problems with getting consistent sample sizes, often resulting in peaks with widely varying heights and areas. Also, if the unknown sample's concentration was significantly lower than the standard's concentration, a short, wide peak was produced and a reliable comparison was not possible. The operating parameters of the GC, the sample sizes, and the phenol standard would then be varied until a suitable combination was found, and analysis would be continued.

All samples, both extraction run and equilibrium phase, were allowed to cool to approximately room temperature principally to allow carbon dioxide bubbles to separate from the liquid but also to allow the liquid density of each analyzed sub-sample to be virtually identical. Sub-samples were drawn from the sample vial with a 10 microliter syringe and injected into the GC injection port. Every effort was made to keep the detector clean and to keep the hydrogen, helium, and air flows as constant as possible. Extreme care was taken when analyzing the equilibrium phase samples. Approximately five GC analyses of each sample were averaged and two standards were run before and after each sample group. Standards were chosen so that phenol concentrations in both the standards and the samples would be nearly the same and would register between 50% and 95% of full scale on the recorder chart. Phenol concentations in the carbon dioxide-rich phase were calculated based on a mass balance of the amount of phenol left in the water phase (measured), the original amount of phenol in the water, and a calculated amount of carbon dioxide placed into the bomb. The actual concentration of phenol in the supercritical phase was not directly measured. Normally, duplicates of extraction run samples were analyzed and an average of the two was considered to be sufficiently accurate. For some of the later runs, when it was clear that several samples from the same run were all representative of the extraction run, individual analyses were grouped together and averaged for a nominal value. This helped reduce the excessive amount of time required for data acquisition and interpretation.

EXPERIMENTAL RESULTS AND DATA ANALYSIS

Introduction

Altogether, fifty-three extraction runs were attempted including forty-eight runs using 10,000 mg/l phenol/water standard and five runs using actual coal gasification wastewater. Of these runs, twenty-three were successfully completed, one counter-current and the remainder co-current. In addition there were seventeen successful phase equilibrium runs at pressures ranging from 1100 to 2800 psi and initial concentrations ranging from 625 to 10,000 mg/l phenol.

The initial intent of this research was to test the feasibility of using counter-current extraction techniques with the two phase, three component system of phenol, water and supercritical carbon dioxide. The extraction equipment was designed and built with the expectation that a number of different parameters could be tested to determine some optimum operating conditions. These parameters included pressure, relative flow rates of solvent and liquid solution, temperature, and column packing. Unfortunately, only one counter-current extraction run was successfully completed after twenty unsuccessful tries. Nine more counter-current flow attempts failed, before it was decided to try co-current extraction tests. The most frequent cause of run failure was the inability to control the carbon dioxide flow within the required degree of accuracy.

Reliability of Data

Throughout this research there are two general catagories, one relating to extraction runs and one relating to phase equilibrium data. A discussion of data reliability must necessarily separate the two, since there is a distinct difference in reliability.

Originally, the phase equilibrium data was gathered to get some idea of the feasibility of extracting phenol from water using supercritical carbon dioxide. Very little information was available in the literature to indicate what would happen with this system or at what conditions an extraction might be optimal. The liquid-liquid-solid ternary phase diagram published by Francis (39), and enlarged in Figure 5, shows that the region of interest, for this research, lies entirely within one percent phenol of the water-carbon dioxide baseline. An attempt was made to experimentally develop a set of equilibrium data for this ternary system at the dilute conditions in question.

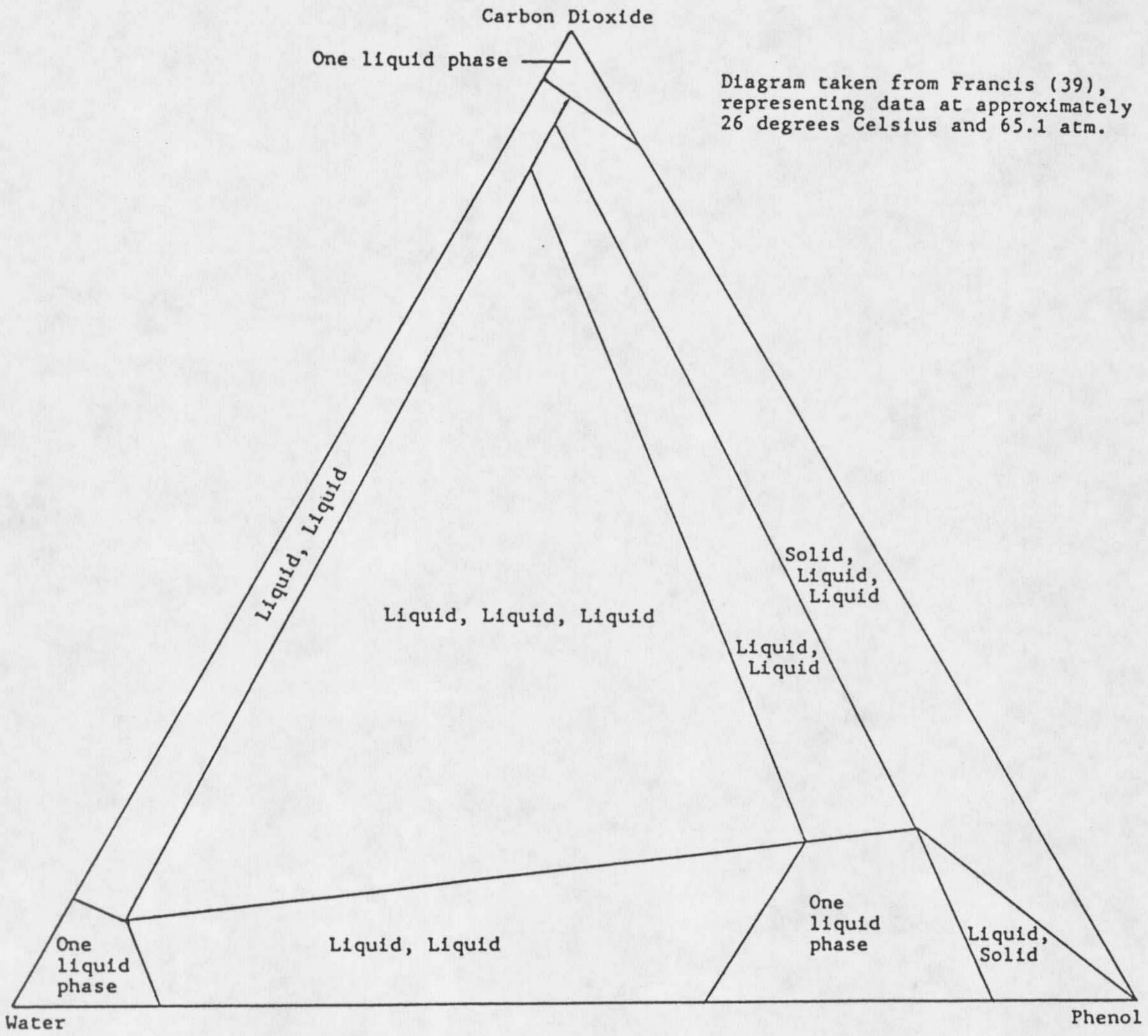


Figure 5. Phenol/Water/Carbon Dioxide Ternary Phase Diagram.

Since the solubility of phenol in supercritical carbon dioxide is a strong function of density and the facilities to analyze high pressure carbon dioxide directly were not available, it was necessary to use the mass balance approach in measuring the phenol concentration in the supercritical fluid (SCF) phase. The actual mass of carbon dioxide can be determined by knowing the volume available to the SCF phase and by knowing the density of carbon dioxide at 40°C and the test pressure. Density data used for these calculations were taken from the temperature-entropy diagram in Perry and Chilton (24). A plot of density versus pressure is shown in Figure 6.

Water samples taken from each equilibrium data experiment were carefully analyzed by gas chromatograph to determine the concentration of phenol in the water rich phase. Using the published experimental density data and the GC phenol concentrations, a phenol concentration was calculated for the SCF phase and expressed as moles phenol per moles carbon dioxide. A number of possibilities existed for the introduction of error in this procedure. Major concerns included the following:

1. GC concentrations were considered to be accurate to within 10% of the actual value. Any error in analysis was compounded by the use of mass balance for determining the mass of phenol in the carbon dioxide phase.

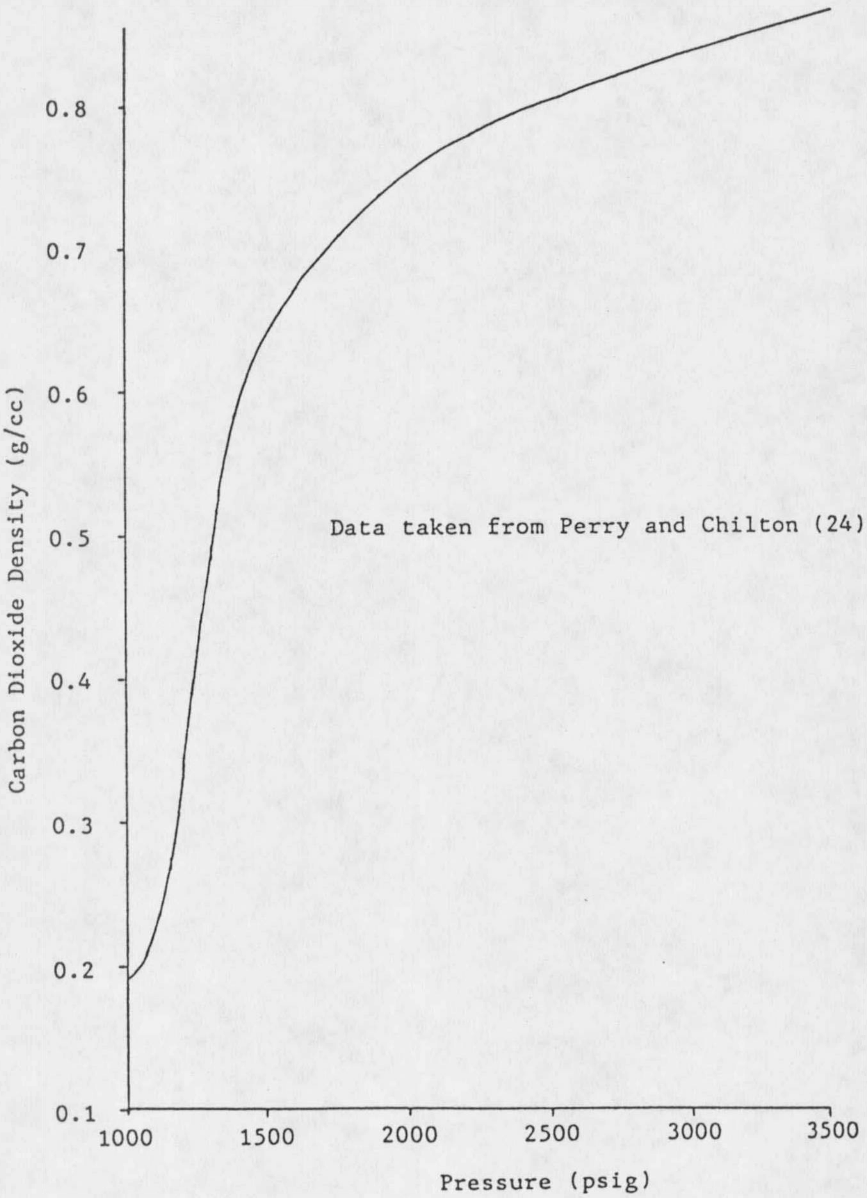


Figure 6. Experimental Pressure and Density Diagram for Carbon Dioxide at 40 Degrees Celsius.

2. The carbon dioxide density, and therefore its mass, was determined by interpolation of the data available from the literature.

3. Since the data was gathered near the critical temperature of carbon dioxide, slight changes in temperature would result in relatively large changes in density. The large amount of mass involved in the test equipment provided a considerable amount of lag time in heat input and temperature change and the temperature measuring apparatus provided a digital readout accurate only to the nearest degree Celsius. Therefore it is difficult to determine the actual margin of error due to measurements that were slightly higher or lower than 40 degrees Celsius.

4. Although a rocker was used to mix the phenol solution and the carbon dioxide, there was no definite way of knowing whether an equilibrium had been reached. As discussed below, residence time was a critical parameter in the extraction runs and could possibly have been a significant factor in the accuracy of the equilibrium data.

The principal concern with the phase equilibrium data is the dependence of an uncertain mass balance to calculate the phenol concentration in the SCF phase. It would be far better to be able to actually measure the concentration in both phases. The equilibrium data does, however, provide a general idea of what to expect during co-current extraction runs, where the approach to equilibrium should be the upper limit. For counter-current extraction the availability of equilibrium data allows the calculation of the number of theoretical trays in a column and the height of an equivalent theoretical plate for a particular set of parameters.

Equilibrium data obtained from this research was used to roughly analyze both the co-current and the counter-current extractions.

Several kinds of data were obtained from the extraction experiments. These included solution and solvent flow rates, temperatures, pressures, and phenol concentrations determined by GC analysis. Solution flow rates were measured very accurately, to within 0.5% of the actual flow, and were subject to only slight variation during any of the valid runs. Solvent flows, on the other hand, were much harder to control, and varied during some runs by as much as 20% above and below the average flow. Since the carbon dioxide flow rates were measured by a wet test meter, which accumulated the total volume of CO_2 during a timed run, an average flow rate was used for analyzing the extraction data. Oven (and column) temperatures were manually controlled to within one degree Celsius of the desired 40^{o}C. System pressure was generally kept within 25 psi of the run's nominal pressure. Extraction runs involving very high rates of carbon dioxide flow usually generated problems with pressure drifting due to excessive cooling near the back pressure regulator. On the last run this problem was virtually eliminated by rearranging the electrical heat tape to more directly heat the back pressure regulator itself. Much higher flow rates were then made possible without causing icing problems.

Phenol/water standards were prepared in the lab and were accurate to within 0.02% of the nominal 10,000 mg/l. This is much more accurate than the estimated accuracy of any one GC analysis, considered to be within 10% of the actual concentration. However, known standards were analyzed before and after any unknowns, and unknown samples were usually analyzed at least twice to minimize any analytical error. By using the GC peak area averages of the standards for reference, and the peak area averages of unknowns for the final concentration, it is believed that the actual concentrations measured and reported in this paper are accurate to within 10% of the true values. The final five extraction runs, using actual coal gasification wastewater, were analyzed on a relative basis. Since there were other phenol derivatives present in this solution, there was some interferences present in the GC charts involving a widening of the peak and secondary peaks riding the main phenol peak's tail. Unknowns, that is, the extracted solution, were analyzed at the same GC setting as the original solution, and the results were expressed as a percentage of the original. Due to the wide differences in peak heights and widths, the accuracy of this data is probably on the order of plus or minus 20% of the actual minus 20% of the actual measurement. In all extraction runs, if any data were considered to be out of the above ranges, the run was considered unusable and the data were not used.

Phase Equilibria

Raw phase equilibrium data are shown in Table 5. These data were then converted to convenient units for comparing concentrations, that is, moles phenol per mole of solvent.

Table 5. Raw Phase Equilibrium Data for the Phenol/Water/Carbon Dioxide Ternary System.

Run	Pressure (psig)	Phenol Concentrations (mg/l) Initial	Final
1	1,210	625	597
2	1,205	1,250	1,180
3	1,205	2,500	2,380
4	1,205	5,000	4,460
5	1,180	10,000	8,500
6	2,330	625	345
7	2,400	1,250	735
8	2,400	2,500	1,320
9	2,355	5,000	2,380
10	2,400	10,000	4,850
11	2,650	1,250	1,135
12	1,880	2,500	1,724
13	1,570	5,000	3,611
14	2,850	5,000	4,154
15	1,100	10,000	9,500
16	1,600	10,000	8,440
17	1,600	10,000	5,940

A summary of these data and the respective distribution coefficients, or equilibrium K-values are shown in Table 6.

Table 6. Mole Fractions of Phenol in Water (x), Mole Fractions of Phenol in Carbon Dioxide (y), and Equilibrium K-values.

Run	Density (g/cc)	Mole Fractions x	y	K-values y/x
1	.345	.000114	.00000913	.0799
2	.340	.000226	.0000235	.104
3	.335	.000456	.0000403	.0884
4	.335	.000854	.000181	.212
5	.300	.00163	.000581	.357
6	.794	.0000661	.0000402	.608
7	.803	.000141	.0000732	.520
8	.805	.000253	.000167	.662
9	.797	.000456	.000375	.822
10	.803	.000929	.000732	.789
11	.817	.000217	.0000275	.126
13	.664	.000692	.000239	.345
14	.830	.000795	.000458	.575
15	.222	.00182	.000849	.469
16	.670	.00162	.00105	.647
17	.670	.00114	.000690	.607

Figures 7 and 8 show three-dimensional plots of that data, viewed from 30 degrees above the pressure-composition plane and rotated horizontally 45 degrees and 135 degrees, respectively. These plots were generated using the SYMAP and SYMVU library routines on the MSU CP6 computer and drawn on a CALCOMP plotter. All seventeen data points were used to generate each plot, showing a general tendency for