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CHARACTERIZATION AND TREATMENT OF COAL-GASIFICATION CONDENSATE WATERS

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Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

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CHARACTERIZATION AND TREATMENT OF COAL-GASIFICATION CONDENSATE WATERS

J.J. Senetar* and C.J. King
(*Ph.D. Thesis)

January 1986

APPLIED SCIENCE DIVISION

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DISCLAIMER

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Characterization and Treatment of Coal-Gasification Condensate Waters

John Joseph Senetar* and C. Judson King

*Ph.D. Thesis

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John J. Senetar

ABSTRACT

This thesis presents work performed to identify the organic constituents in coal-gasification condensate water, along with consideration of the alternatives for condensate water treatment. The characterization experiments performed were primarily limited to a condensate water received from the Lurgi slagging fixed-bed gasifier at the Morgantown Energy Technology Center (METC); however, the analyses of one condensate water sample from the Grand Forks Energy Technology Center (GFETC) and one sample from the Great Plains Gasification Associates (GPGA) gasifier are also included.

The characterization results indicated almost complete identification of the compounds contributing to the chemical oxygen demand (COD), total organic carbon (TOC), organic sulfur, and organic nitrogen measurements in the METC condensate water. Thiocyanate was found to contribute significantly to the COD, organic nitrogen, and organic sulfur measurements of the condensate sample. In addition, polysulfides were also found to contribute to the COD and the organic sulfur measurements. Low-molecular-weight solutes (acetonitrile, acetone, and methanol) were not found to be appreciable in the METC sample but were found to a much greater extent in the GPGA and GFETC samples.

Equilibrium distribution coefficients from water into methyl

isobutyl ketone (MIBK) were determined for many of the condensate water solutes. In addition, other extractants including benzophenone, tributyl phosphate (TBP), tributyrin, furan, and 4-methyl cyclohexanone were investigated. TBP was found to yield the highest distribution coefficients for the condensate solutes and to be potentially attractive economically for condensate treatment.

Adsorption experiments revealed that both activated carbon and Amberlite XAD-7 (Rohm and Haas) were effective for removal of catechol and 5,5-dimethyl hydantoin from water; however, only Amberlite XAD-7 was easily regenerable with solvents after adsorption of catechol.

Both strong-base and weak-base anion-exchange resins were investigated for thiocyanate recovery. Use of weak-base resin was found to offer potential advantages over the strong-base resin.

The relative merits of various physicochemical treatment methods are analyzed, as well as the effect that ordering of various unit operations has on treatment. Use of byproduct ammonia for regeneration of solvents and adsorbents may be attractive and warrants futher research. Also, a two-stage quench design was found to offer economic advantages over a one-stage quench, presenting new opportunities for condensate treatment.

DEDICATION

To my wife Caroline

ACKNOWLEDGEMENTS

Over the course of my stay at Berkeley I have benefited from interactions with the faculty, staff, and students. These individuals are too numerous name here, however, there are some special people I would like to formally thank.

First, I acknowledge C. Judson King for his chemical engineering insight and assitance throughout my work and in the preparation of this thesis. It has been a pleasure and a rewarding experience to work with him both during this work and while obtaining my masters degree. To his titles of Dean, Professor, and Doctor, I add the title of friend.

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Mark Prausnitz, Ronlyn Goo, and Sharon Hwang all assisted in taking data. Not all of their data made it into this final report; however, their assistance was much appreciated. Mark gathered much of the data on adsorption and ion exchange presented in Chapter III.

I thank the 24 or so odd coworkers (and some of them were) that made up Professor King's research group during my masters and doctorate research. Their cooperation and sense of humor made the work environment much more enjoyable. Tony Garcia and Bill Rixey deserve special mention for their assistance in providing references and materials for the adsorption and ion exchange portion of this work. Thanks goes to Terry Grant for acting as a sounding board for ideas and providing helpful suggestions. Also, thanks goes to Tarric El-Sayed for his help and for the times we spent sharing the woes of experimental

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Ann Harrington was helpful at squeezing me in for unscheduled appointments and getting me through the mounds of bureaucratic paperwork. I appreciated her help and encouragement.

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CHAPTER I

BACKGROUND, PROJECT DESCRIPTION AND GOALS

I-A. Condensate Waters - Sources and Composition

I-A-1. Sources of Condensate Water

I-A-1a. Synthetic Fuels

Large scale use of synthetic fuels dates back to the early 1800's in London, where coal was first used to produce illuminating gas for home and street lighting (Perch, 1980). This gas had low heating value (550 BTU/SCF) and was produced by subjecting coal to destructive distillation in absence of air. Since then alternative techniques for obtaining both liquid and gaseous fuels from coal have been developed. Much progress in this area was accomplished by Germany during World War II. Today large scale coal conversion plants are in operation at Sasolburg, South Africa and Kosovo, Yugoslavia for the production of both synthetic liquid and gaseous fuels. The history and current state-of-the-art for obtaining synthetic fuels from coal is discussed by Perch (1980), Kalfadelis and Shaw (1980), and Probstein and Hicks (1982).

About 90% of the energy consumed in the United States today is derived from fossil fuels. Crude oil, of which over 30% is imported from other nations, supplies over 40% of the total energy consumption for the United States. Natural gas and coal contribute about 25% and 23% of the energy consumed, respectively (Energy Information Administration, 1985a). Coal represents 80% of the world's proven energy resources, with the United States possessing about 26% of these reserves (Probstein and Hicks, 1982). Oil shale deposits in the western U.S. and tar sand deposits in Canada are large energy resources that have yet to be exploited.

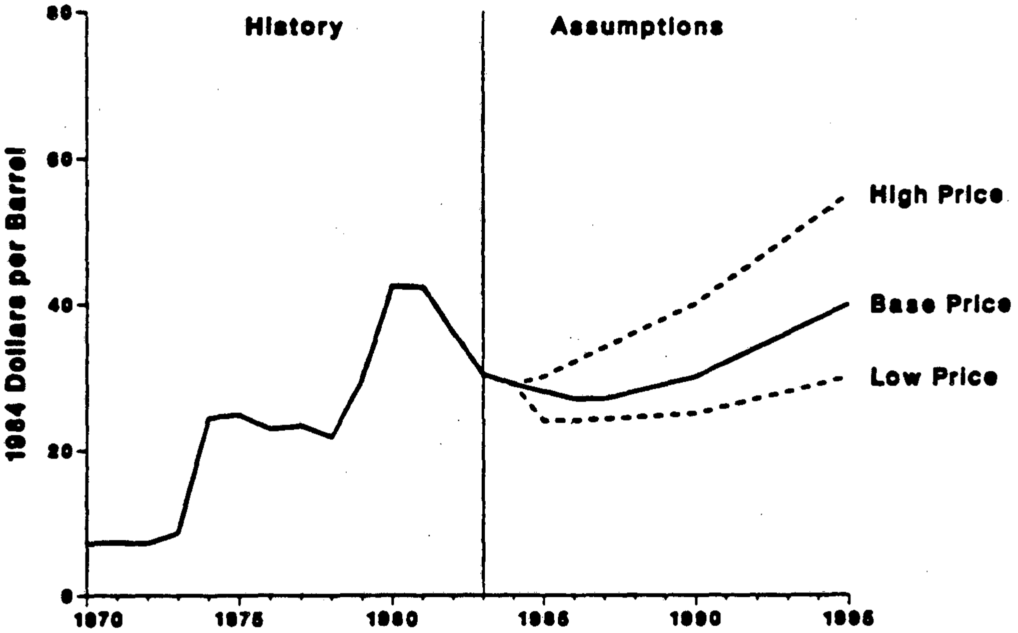
The interest in the United States for utilizing synthetic fuels has gone through several cycles of activity followed by abandonment. The most recent surge of interest was brought on by the Arab Oil Embargo of 1973, which led to increased crude oil prices and demonstrated the dependence of the U.S. on foreign crude oil exports. In the late 1970's to the early 1980's both the U.S. Government and private industry, primarily oil companies, funded research that utilized alternative energy resources, particularly coal. Research efforts led to the building of several pilot plants in the U.S. for coal liquefaction, coal gasification, and oil shale retorting. Today few of these projects are in operation.

Figure I-1 presents world oil prices from 1970 through 1983 with projections out to 1995, illustrating the decrease in U.S. crude oil prices since 1980. According to the Energy Information Administration (1985b), the decrease in crude oil prices since 1980 has been a result of the weaker-than-expected oil demand, the strong U.S. dollar in non-U.S. markets, and the sustained increase in oil production by non-OPEC oil producers. The decrease in crude oil demand has been attributed to increased automobile efficiency, conservation measures, and fuel switching (i.e, converting from fuel oil to natural gas for heating).

Nevertheless, crude oil prices are expected to increase over the next decade, and by 1995 crude prices are predicted to be nearing the price reached in 1980. Such a trend is likely to lead to a crude oil price at which production of synthetic fuels will again become more

FIGURE I-1

WORLD OIL PRICES, 1970 - 1995 (Energy Information Administration, 1985b)



actively pursued. It should be pointed out that the crude oil prices have dropped to below $20/barrel in January 1986, lower than that predicted in Figure I-1.

At this time, the Great Plains Gasification Plant is the only plant constructed in the United States to produce synthetic fuels for sale on the open market; however, the project was halted in 1985 due to a lack of financial support. Even if the Great Plains plant were to remain operating, the use of coal for synthetic fuels in the U.S. was expected to remain less than 1% of the of the annual U.S. coal consumption through the year 1995 (Energy Information Administration, 1985b).

Table I-1 presents a comparison of the carbon-to-hydrogen (C/H) weight ratios of various fossil fuels and derived products. The data demonstrate that the desired fuel products have a higher C/H ratio than the fossil fuels from which they are derivied. Crude oil has the higher H/C ratio of the fossil fuels and therefore requires the least upgrading to obtain desirable fuel products. Obtaining usable fuel from both oil shale and tar sands is complicated, despite the relatively high H/C ratio for these resources, since they typically are composed of nearly 85 wt% inorganic minerals.

The goal of synfuel processes is to increase the H/C ratio of the fossil fuels in order to produce directly usable fuels and/or products that could be further upgraded to usable fuels. Both coal gasification and oil shale retorting involve pyrolysis to obtain low-molecular-weight hydrocarbons. The heat necessary for pyrolysis is supplied both from the introduction of air (or oxygen) to promote combustion, and by the introduction of high-temperature steam. Steam not only provides the heat for pyrolysis but also is a necessary source of hydrogen to

TABLE I-1

HYDROGEN-TO-CARBON MASS RATIO FOR VARIOUS FUELS

Fuel	H/C Mass Ratio
Bituminous Coal	~0.07
High-Grade Oil Shale*	~0.13
Crude Oil	~0.11
Gasoline	0.17
Methane	0.33

---

* Approximately 85 % mineral content.

increase the H/C ratio of the products. The energy balance for the processes requires that steam be introduced in excess of the stoichiometric amount required for conversion; therefore, both coal gasification and oil shale retorting often consume larger quantities of steam than necessary for conversion. Also, some excess steam is necessary to take advantage of the water-gas shift reaction. Steam not consumed in the process is recovered from the gasifier gases by cooling, creating large quantities of condensed water, commonly referred to as condensate water.

The Lurgi slagging fixed-bed gasifier, the type built at Great Plains, is reported to operate closest to the stoichiometric water requirement of the currently proposed gasifiers. Condensate water production at the Great Plains gasification plant was measured at near 3.75 MM gal/day (almost 1 MM lb/Hr) for gas production at 485 MM SCF/D (Bossart, 1985).

The remainder of this discussion is limited to coal gasification.

I-A-1b Coal Gasification

Probstein and Hicks (1982) discuss several processes that have been developed for coal gasification. These processes are designed to produce gases of varying heating value, depending on the mode of operation. Gasifiers operating with air rather than oxygen produce product gases that have lower heating value than gasifiers operating with purified or enriched oxygen. Gasifier gases can be further purified to yield gases with a higher heating value, or upgraded to produce methane, substitute natural gas.

TABLE I-2

IMPORTANT REATCIONS GOVERNING COAL GASIFICATION*

Conversion and Synthesis Reactions

$C + H_2O = 1/2\ CO_2 + 1/2CH_4$ (Gasification)

$C + H_2O = CO + H_2$ (Gasification)

$CO + H_2O = CO_2 + H_2$ (Water-Gas Shift)**

$CO + 3\ H_2 = CH_4 + H_2O$ (Methanation)**

$CO + 2\ H_2 = CH_3OH$ (Methanol)**

$C + CO_2 = 2\ CO$ (Boudouard)

Pollutant-Forming Reactions

$1/2\ N_2 + 3/2\ H_2 = NH_3$**

$H_2 + S(g) = H_2S$**

$S(g) + O_2 = SO_2$**

$1/2\ N_2 + O_2 = NO_2$

$1/2\ N_2 + 1/2\ O_2 = NO$

$6\ C + 3\ H_2 + 1/2\ O_2 = C_6H_5OH$

---

* Adapted from Probstein and Hicks (1982).

** Equilibrium favors products at lower temperatures.

Gasifiers typically operate at temperatures between 815 C and 1925 C. Table I-2 presents a summary of some of the important reactions that occur in coal gasification. As indicated in Table I-2, lower temperature operation favors the formation of some of the products, most notably the pollutant-forming reactions for ammonia, hydrogen sulfide, sulfur dioxide, and phenol. High-temperature operation yields more favorable equilibrium for the primary gasification reactions, but also increases the formation of NO_x. The effect of gasification temperature on the extent of phenol formation has been experimentally studied by Nakles and Fillo (1983), who observed that phenolic compounds decomposed rapidly at high temperature, and that the decomposition rate was enhanced by the presence of the hot coal char. As will be discussed later, phenolic compounds are the major constituent in the coal-gasification condensate waters. Therefore, high-temperature gasification processes produce condensate waters which contain less phenolics and thus require less treatment than do condensate waters from low-temperature processes. A comparison of waters generated by several high-temperature and low-temperature gasifiers is presented by Mohr and King (1983).

Holt (1983) discusses the environmental issues associated with the design configuration of coal gasifiers. Gasifiers have been designed to operate in fluidized-bed, entrained-bed, or fixed-bed modes, and the resulting temperatures and residence times have a large impact on the formation of pollutants. Examples of fluidized-bed gasifiers are the Winkler, Westinghouse, and IGT 'U' Gas processes. The Koppers-Totzek, Shell, and Texaco processes operate with entrained beds.

In the fluidized-bed gasifiers, steam and oxygen are introduced at the bottom of the gasifier and the coal is fed in from the top. Large vapor flow rates and backmixing lead to a uniform temperature profile throughout the gasifier. Entrained-bed gasifiers operate with coal and gas moving cocurrently; however, the temperature profile of the gasifier is uniform throughout due to the large ratio of steam to coal. The gases exiting both the fluidized-bed and the entrained-bed gasifiers are at a high temperature, necessitating recovery of the sensible heat. The high exit temperatures lead to less pollutants being present in the effluent gases and consequently less contaminated condensate water than fixed-bed processes. However, the larger steam consumption for these processes leads to larger volumes of condensate water requiring treatment.

The so called "fixed-bed" gasifiers operate with a dense coal bed to which fresh coal is added at the top and from which ash is removed at the bottom. These gasifiers operate with steam and air being passed upward through the coal bed. A much lesser flow of gases (steam and oxygen) per quantity of coal is used compared to the fluidizized-bed or entrained-bed gasifiers. The fixed-bed gasifier differs from the other gasifiers in that the gases exit the fixed-bed gasifier at a lower temperature than the inlet steam. Examples of fixed-bed gasifiers are the Lurgi-Dry Ash, British Gas Corporation (BGC)/Lurgi Slagging, Kilngas, Chapman, and Wellman-Galusha processes. The Lurgi-Dry Ash and the BGC/Lurgi Slagging gasifiers are the only large commercial gasifiers in operation today.

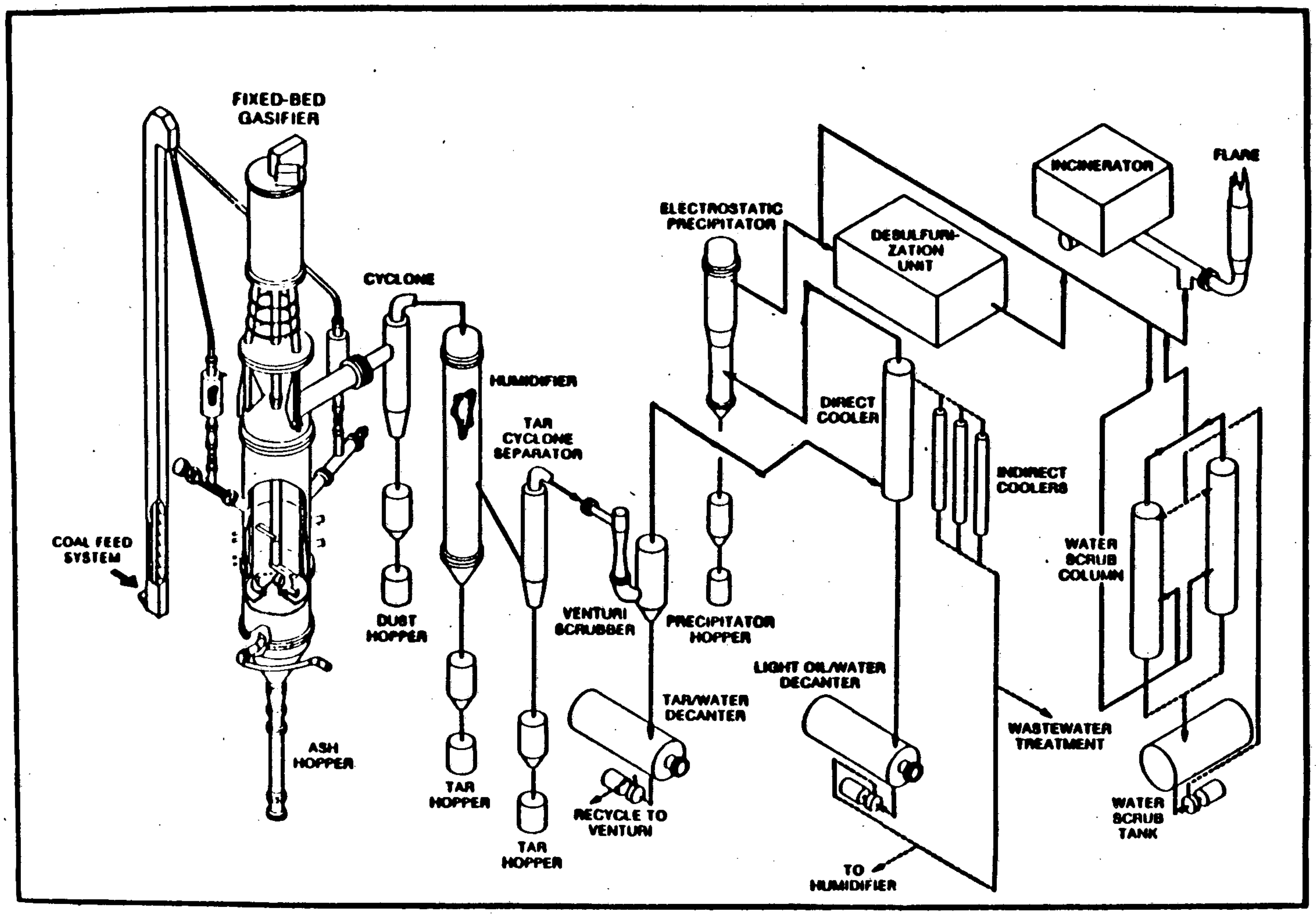
The Lurgi-Dry Ash and BGC/Lurgi Slagging gasifiers differ slightly in configuration. The effluent gases from both gasifiers exit from the lowest temperature zone of the gasifier, leading to the presence of tars and oils in the effluent gases. The original Lurgi version maintained the temperature in the highest temperature zone below the ash fusion temperature, slagging temperature, by the introduction of excess steam. The BGC version of the Lurgi gasifier operates at the slagging temperature of the coal with only the amount of steam necessary for gasification. A higher temperature in the bottom of the BGC/Lurgi gasifier leads to faster reaction rates and an increase in throughput (3 to 4 times) compared to the original Lurgi design. Since the BGC version has a lesser steam consumption it produces less condensate water per amount of coal gasified and therefore lowers the costs associated with condensate treatment. The BGC/Lurgi gasifier is commonly referred to as a slagging fixed-bed gasifier.

Slagging fixed-bed gasifiers have been built for experimental studies at the University of North Dakota Energy Research Center (formerly the Grand Forks Energy Technology Center, GFETC) and the Morgantown Energy Technology Center (METC).

Figure I-2 presents a diagram depicting the Lurgi slagging fixed-bed gasifier and its associated gas-cleanup system at METC (Wachter, 1983). In this process, the gases exiting the gasification reactor are first passed through a cyclone to remove entrained particles, and then sent through a series of operations to remove the high-molecular-weight compounds, or tars. Cooling, or quenching, of the gases occurs in the direct cooler, where the gases enter at approximately 142 C and are cooled to near 55 C through direct contact with a recycled water stream. Unconverted steam in the gas is condensed in the direct cooler to produce condensate water, of which part is recycled to the direct cooler. In this particular process the temperature of the gases exiting

FIGURE I-2

METC GASIFIER AND GAS CLEANUP SYSTEM (WACHTER, 1983)



the direct cooler was set at 55 C due to a temperature limitation for the downstream Holmes-Stretford desulfurization unit. The gases are next passed through an electrostatic precipitator to remove fine particles before desulfurization. Indirect coolers operate with cooling tower water to remove heat from the recycled condensate so as to meet the specified exit gas temperature. The condensate water that is not recycled to the direct cooler is either recycled to the humidifier or removed as condensate water for treatment. The ratio of water recycled to the direct cooler to that sent to condensate treatment is reported to be about 700 to 1 (Bossart, 1985).

I-A-2. Composition of Coal-Condensate Waters

Presented in Table I-3 are typical water-quality parameters measured for coal-gasification condensate waters and the typical range of values. The values reported are based on the Hygas, Lurgi, and Synthane process effluents, where the larger numbers are more characteristic of the condensate water obtained from a Lurgi-type gasifier. The condensate waters contain both large amounts of dissolved ammonia and acid gases (i.e., carbon dioxide, hydrogen sulfide, hydrogen cyanide) and ionic species such as thiocyanate in a highly buffered solution at pH 7.8 to pH 9.3., depending on the ratio of ammonia to acid gases. The large amount of dissolved carbon dioxide (as bicarbonate and carbonate) is reflected by the high measured alkalinity for the condensate water. The other acid gases are present in much lesser amounts. The Kjeldhal nitrogen measurements include both nitrogen present in organic solutes and that in the dissolved ammonia form, and therefore should be larger than the ammonia nitrogen measurements. The

TABLE I-3

TYPICAL WATER QUALITY PARAMETERS FOR COAL GASIFICATION CONDENSATE WATERS BASED ON HYGAS, LURGI, AND SYNTHANE PROCESS EFFLUENTS

Parameter	Typical Range
pH	7.8 - 9.3 (1)
Alkalinity, as $CaCO_3$ (mg/L)	17,300 (2) (Lurgi Only)
Nitrogen	
Kjeldhal (mg/L)	4480 - 11,200 (3)
Ammonia (mg/L)	4480 - 11,200 (1)
Cyanide, Free (mg/L)	0.07 - 0.6 (1)
Sulfide (mg/L)	138 - 400 (1)
Thiocyanate (mg/L)	22 - 200 (1)
Phenols (mg/L)	710 (1) - 13,300 (4)
Chemical Oxygen Demand (mg/L)	4050 (1) - 46,700 (4)
Total Organic Carbon (mg/L)	4190 (1) - 10,300 (4)
Oil and Grease (mg/L)	840 - 910 (1) (Lurgi Only)
Total Dissolved Solids (mg/L)	2500 (2) (Lurgi Only)

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(1) From Bhattacharyya et. al. (1982).

(2) Probstein and Hicks (1982).

(3) Estimate based on ammonia analysis presented here.

(4) Based on the analysis of Mohr and King (1985) presented in Table I-4.

difference between these two measurements is not great since few solutes containing organic nitrogen are present in the condensate waters.

The measured total organic carbon (TOC) and chemical oxygen demand (COD) reflect the large amounts of dissolved organic compounds. The organic compounds are primarily phenolics in the range of 710 to 6600 mg/L. It should be noted that the standard method of quantifying phenolic compounds is a colorimetric procedure that fails to detect para-substituted phenols, such as p-cresol (Luthy, 1978). Additionally, the condensate waters contain trace quantities of heavy metals, typically < 1 mg/L (King et. al., 1981; Probstein and Hicks, 1982).

Nichols and Green (1981) present a list of several hundred organic compounds that have been identified in coal-gasification streams, most at trace levels, ranked both by health hazard and environmental hazard. Most of these compounds have the potential of ending up in the condensate water. Futhermore, many of the compounds that are present to a greater extent also appear on the EPA Priority Pollutant List (Keith and Telliard, 1979), thus demonstrating both the variety of compounds and the importance of controlling their release to the environment.

Presented in Table I-4 are the results of Mohr and King (1983) for the analysis of four different condensate water samples obtained from the Grand Forks Energy Technology Center (GFETC) gasifier. The analyses of the low-molecular-weight compounds (i.e. acetone, methanol, and acetonitrile) in Run RA-106 were obtained from a joint effort of this work and that of Mohr. The results were combined for a joint presentation at the Third Biennial Synfuels Wastewater Workshop (Mohr, Senetar, and King, 1983).

Table I-4 demonstrates that the phenolic compounds comprise a large

TABLE I-4

QUANTITATIVE ANALYSIS OF GFETC CONDENSATE WATERS[a] (Mohr and King, 1983)

GFETC Run No.:	RA-78	RA-97	RA-106	RA-120
Sample age interval (days)[b]:	150-500	40-150	1.7-38	0.7-110
Compounds	**Concentrations (mg/L)**			
Hydroxybenzenes:				
Phenol	4,750	7,250	3,450	4,300
Cresols	2,850	3,750	2,140	2,350
Xylenols	450	470	430	410
o-methoxy phenol	260	450	165	260
p-hydroxy acetophenone	50	35	5	ND
Dihydroxybenzenes:				
Catechol	990	860	40	2
4-Methyl Catechol	610	500	20	ND
Resorcinol	60	28	2	ND
Hydroquinone	35	24	1	ND
Hydantoins:				
5,5-Dimethyl Hydantoin[c,e]	1,720	300	460	165
	(660)	(150)	(230)	(40)
5-Methyl Hydantoic Acid	95	130	ND	10
5-Methyl Hydantoin	135	40	ND	35
Low-Molecular-Weight Solutes:[d]				
Methanol	---	---	1,050	---
Acetonitrile	---	---	365	---
Acetone	---	---	505	___
Chemical Oxygen Demand (mg/L)	34,900	46,700	22,900	23,400

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a. Estimated Precision: ±5 %.

b. No change in concentration was observed over this time interval with exception of dimethyl hydantoin concentration.

c. This is the concentration at long sample ages. The value in parentheses is the estimated concentration when the sample was removed from the gasifier. Acetone decreases and dimethyl hydantoin increased in concentration with time. The concentrations of all of the other solutes did not change with time and were the same in the sample portions which were stored at pH 8.5 and pH 2.

d. From Mohr, Senetar, and King (1983).

e. The concentration in parentheses is for the sample stored at pH 2.

portion of the organics in the condensate water and account for the majority of the identified chemical oxygen demand (COD) of the samples. Phenolic compounds are recognized pollutants and appear on the EPA Priority Pollutant List. Phenolics have long been a problem in wastewater treatment, dating back to the early days of coal distillation. They are also present in coke-oven wastewaters.

Little is known of the health and environmental hazards presented by the hydantoins. Hydantoins have been used in the pharmecutical industry and also for the production of synthetic resins, consumer products, such as hair sprays, and photographic film (Bateman, 1980). Ware (1950) presents a review of the chemistry of hydantoins and their derivatives. Hydantoins can be hydrolyzed under acidic conditions to yield hydantoic acids. Olson et. al. (1983) report other hydantoin derivatives that have been identified as being present in GFETC condensate water samples, in addition to those listed in Table I-4.

The relative and total amounts of the phenolics and hydantoin found in the condensate waters vary between samples. The extent that the low-molecular-weight compounds vary between samples was not investigated by Mohr; however, the presence of these and other volatile polar organics in gasification condensate waters has been confirmed by White and Schmidt (1978).

I-B. Treatment of Coal-Condensate Waters

I-B-1. Potential Fate and/or Reuse of Condensate Waters

The condensate waters contain a variety of compounds that have the potential of causing detrimental effects to the environment if the water were discharged to the surroundings without sufficient treatment. Even after treatment there remains the decision as to whether the water should be released to the surroundings or recycled within the process. The relative merits of recycling condensate water in coal gasification has been discussed by Witmer (1983) and have been a topic of discussion at various synfuels syposiums. A literature review on the general topic of water recyling in industrial processes has been presented by Matthews (1980).

In the discusssion that surrounded the Third Biennial Synfuels Wastewater Workshop (1983), it became evident that public perception of the impact of releasing water to the environment posed a barrier to the construction of synthetic fuels plants, regardless of whether or not the plant was to be designed to meet current EPA standards. The prevalant opinion was that a coal gasification plant should operate with essentially complete water recycle so as to promote being labeled as having "zero discharge" of aqueous effluents. In light of the publicity surrounding recent releases from chemical plants and the increased awareness of the public concerning water quality, recycling water is even more favored.

The need for water recycle is brought on not only by environmental issues but also by the large consumption of water required for synfuels conversion processes. To save the cost of shipping coal, coal gasification plants are considered likely to be constructed in areas close to the coal deposits. Coal deposits in the Western United States are located in arid regions where water resources are limited. In these cases water recycle would be necessary for plant operation. Water recycled within a process would not have to meet the stringent criteria for discharge, and therefore presents the possibility of lessening the treatment cost for the condensate water.

Table I-5 presents potential advantages and disadvantages of selected reuse options as presented by Witmer (1983). Of the options listed in Table I-5, the treatment of condensate water for cooling tower make-up has been the most actively investigated. Seufert et. al. (1979) report that treated condensate water could supply up to 54% of the cooling tower makeup necessary for a Lurgi type gasifier. Galegher et al. (1985) and Stetter et al. (1984) have performed studies on the use of extracted and steam stripped condensate water as makeup for a cooling tower. The results demonstrated a build up of hydantoins and inorganic compounds (e.g., thiocyanate) in the cooling tower over time. Willson (1983) reported a build up of 1.7 wt% 5,5-dimethyl hydantoin in a cooling tower blowdown, a ten-fold increase in the concentration over the incoming make-up water. Stetter et al. report that no cytotoxic or mutagenic activity was observed for either the condensate water or the cooling tower blowdown at a 10-fold increase in concentration of nonextracted and nonstripped solutes. Also, the results of Galegher et al. (1985) demonstrate that fouling of heat exchange surfaces was not a problem when using materials constructed from stainless steel.

Re-injection of the condensate water back into the gasifier would require essentially no treatment of the condensate, assuming that the compounds in the condensate would decompose in the gasifier and not build up in the condensate water recycle. The extent to which condensate could be recycled directly back to the gasifier as water depends on the energy balance for the gasifier. The cost of treatment would be the energy required to convert the condensate water back into steam. Gasifiers that operate at lesser steam/coal ratios possess the

TABLE I-5

SELECTED WASTEWATER "REUSE" OPTIONS (Witmer, 1983)

OPTION	POTENTIAL ADVANTAGES	POTENTIAL DISADVANTAGES	UNCERTAINTIES
REINJECTION INTO CONVERSION PROCESS	• "ZERO" DISCHARGE • DECREASES WATER USE • CAN CONSERVE SENSIBLE HEAT • LITTLE TREATMENT REQUIRED	• CONCENTRATION STEP MAY BE REQUIRED TO PRESERVE WATER BALANCE • PROCESS CHANGES MAY BE REQUIRED TO ACCOMMODATE	• RELIABILITY AND COST • SOME MATERIALS MAY FAVOR RECYCLE LOOP, MAKING PURGE NECESSARY • NATURE OF SOLID WASTES MAY BE MODIFIED
MAKE-UP FOR COOLING TOWERS	• "ZERO" DISCHARGE • DECREASES WATER USE	• SIGNIFICANT PRETREATMENT MAY BE REQUIRED • MAY NOT BE APPLICABLE ON YEAR-ROUND BASIS	• RELIABILITY AND COST • CONTAMINANTS IN DRIFT MAY PRESENT PROBLEM • CORROSIVE NATURE AND SPARINGLY SOLUBLE CONSTITUENTS MAY PRESENT DIFFICULTY
MAKE-UP FOR FLUE GAS DESULFURIZATION UNIT	• SAME AS ABOVE • COULD IMPROVE FORCED OXIDATION OF SLUDGE	• TRACE METAL PPT MAY ADVERSELY AFFECT LIME REACTIVITY	• TRACE ELEMENTS IN SLUDGE MAY PRESENT PROBLEM
WET-DOWN FOR DUST CONTROL AND IRRIGATION	• "ZERO" DISCHARGE • ASSISTS IN CONTROL OF FUGITIVE EMISSIONS • ABETS REVEGETATION EFFORT	• SIGNIFICANT PRE-TREATMENT REQUIRED • INTRUSION OF TRACE ELEMENTS AND REFRACTORY ORGANICS INTO ECOSYSTEM AND AQUIFERS	• EXTENT OF NATURAL "DETOXIFICATION" OF CONTAMINATED WASTES
BOILER FEEDWATER	• "ZERO" DISCHARGE	• SIGNIFICANT TREATMENT AND DEMINERALIZATION REQUIRED	• COST
FEED FOR SANITARY SYSTEM	• SAVE POTABLE WATER	• TREATMENT REQUIRED TO CONTROL COLOR AND ODOR, ADDITIVES MAY WORK	• COST BENEFIT • COLOR AND ODOR MAY CAUSE OBJECTIONS • EFFECT ON BIOTREATMENT PLANT

greater potential for utilizing reinjection of condensate into the gasifier. Nevertheless, considerable concentration would be necessary in order to preserve a water balance.

Conversion of the condensate water to steam before recycling back to the gasifier would avoid the energy balance constraints. However, the high concentration of dissolved salts and organic compounds in the condensate water makes it unlikely that the condensate water could be converted into steam without considerable pretreatment. Even water obtained from natural waterways often requires treatment to remove dissolved solids before use as boiler feed water. The potential fouling of heat exchange surfaces greatly limits the possibilities for this mode of direct recycle.

The possibility of using condensate as make-up for a flue gas desulfurization unit is highly dependent on the desulfurization process (i.e., the water needs and the water quality necesssary). Other options such as using condensate for dust control, irrigation, and feed for sanitary water would require extensive treatment, for the reasons described above. Also, such use would not be attractive to the public.

I-B-2. Treatment Alternatives

Table I-6 lists various treatment methods that have been suggested for condensate treatment. The advantages and disadvantages of these processes are discussed below.

I-B-2a. Biological Treatment

Biological treatment has been the most widely used procedure for treating industrial wastewaters prior to discharge (Mulligan and Fox,

TABLE I-6

PROPOSED CONDENSATE WATER TREATMENT METHODS

Non-Recovery Methods

- Biological Oxidation
- Chemical Oxidation
    - Incineration
    - Ozonation
    - Wet Air Oxidation
- Oxidative Coupling
    - Aerobic Coupling
    - Enzymatic Coupling

Recovery Methods

- Adsorption
- Evaporation
- Membrane Separations
- Solvent Extraction
- Stripping

1976). Biological treatment has the advantage of achieving low effluent levels for a wide variety of organic solutes. Various investigators have carried out studies evaluating biological oxidation for synfuels waterwaters (e.g., Neufeld et al., 1984; Luthy et al,1980).

Although it is widely used, biological treatment has several disadvantages. First, some compounds are refractory and therefore are not subject to biological degradation. Second, biological oxidation is limited to low concentrations of organics, and thereby may require substantial dilution of the aqueous streams before treatment. Organic solutes, such as phenol, and inorganic solutes, such as ammonia, are often lethal to microorganisims at the concentrations present in the condensate water. Third, even for feeds with low solute concentrations, biological treatment can be upset by changes in composition due to process fluctuations and/or changes in operating conditions. Lastly, biological treatment often requires large residence times (i.e., on the order of a day) and therefore requires large holding tanks or ponds to be constructed. Since typical synfuels plants are envisioned as producing near 1 MM gal/hr of condensate water, holding tanks would have to be very large indeed.

Due to its limitations, aqueous streams frequently require substantial pretreatment before biological oxidation. Pretreatment can involve costly operations such as pH adjustment, addition of lime and alum, and stripping. It should be noted that both adsorption and solvent extraction, which are competing processes, have been found to be effective means for the removal of organic solutes prior to biological treatment. Also, adding activated carbon to a biological oxidation process has the potential to dampen out the effects of upsets and allow treatment of more concentrated streams.

I-B-2b. Other Oxidative Techniques

Other oxidative techniques such as incineration, wet air oxidation, and ozonation have been investigated for wastewater treatment. Although these techniques have been shown to be effective treatment methods in specific cases, they tend to be extremely energy intensive. Also, equipment costs for processes such as wet air oxidation are very high. Both incineration and wet air oxidation allow some energy recovery when treating liquid streams with higher organic content; however, the concentrations of the organic solutes in the condensate water are too low for any energy benefits to be derived from these processes. An advantage of the oxidative techniques is that they have the potential of being complete treatment processes in themselves for the organic solutes. However, there still may be a need for further treatment for some of the inorganic solutes. Other treatment methods either require pretreatment or are limited to the degree of treatment obtainable. The higher energy costs for these processes can be tolerated to some extent at the benefit of eliminating additional equipment and the associated operating costs.

A process for incineration of condensate water has been presented by Leinhard and Winkler (1983). In this process, the condensate is first evaporated to yield approximately 90% vapor and 10% liquid. The vapor and liquid streams are then sent to separate incinerators. The salts are reported to remain in the liquid stream, thereby necessitating scrubbing of only those gases exiting from the liquid incinerator, the smaller of the two streams. The authors did not present any economics or report on the energy consumption of the process; however, the initial evaporation step would itself consume much energy. The process is reported to be commercially available from Lurgi.

Wilhelmi and Knopp (1979) discuss the application of wet air oxidation for treatment of liquid industrial wastes. The operation is described as taking place under high pressure at a temperature between 177 C to 315 C, taking advantage of the higher solubility and diffusivity of oxygen in aqueous solutions at higher temperatures. Wilhelmi and Knopp present experimental data for 1 hour wet oxidations of phenol and 2,4-dimethyl phenol (2,4-xylenol) at both 275 C and 320 C. Over 99.9% destruction of both compounds was observed under both conditions, with starting concentrations of phenol and 2,4-dimethyl phenol of 10.0 g/L and 8.22 g/L, respectively.

Wet air oxidation, as a liquid-phase process, has the advantage over incineration in that it is not necessary to supply the latent heat of vaporization for the aqueous stream. However, the equipment costs are much higher since the process operates at high pressure and requires corrosion resistant materials. Drummond (1984) presents results of a preliminary investigation of wet air oxidation to treat a sample of GFETC condensate water. The results indicated that the most successful oxidation (>99 % removal of phenols) occurred with water that had previously been ammonia-stripped. Unstripped water gave a much lesser removal of phenol (65 %). Wilhelmi and Knopp report that acid gas solutes such as cyanide and thiocyante can be effectively converted into carbon dioxide, ammonium sulfate, and sulfuric acid. Apparently ammonia is not oxidized to NO_x, as it could be in an incineration process. The effectiveness and economics of wet air oxidation require further evaluation.

Hackman (1978) provides a review of chemical oxidation techniques, including ozonation, for the treatment of industrial wastewaters. Drummond (1984) reports on ozonation experiments directed toward treatment of condensate water. Experimental results demonstrated that both phenol and 5,5-dimethyl hydantoin were susceptible to ozonation; however, destruction of the compounds was not rapid even when relatively large amounts of ozone were employed. Furthermore, experiments demonstrated that ozonation was not able to lower significantly the contaminants remaining in a GFETC condensate water sample which had previously undergone dissolved-gas stripping, solvent extraction, and biochemical oxidation. In light of these results, it seems doubtful that ozonation could become an attractive alternative for condensate water treatment.

I-B-2c. Oxidative Coupling

Lim and coworkers (Lim et. al.,1983; Chin et. al., 1985) discuss a process which ultilizes aerobic coupling of phenolic compounds for condensate water treatment. Their proposed process involves the addition of copper (II) chloride as a catalyst to react phenolic compounds to form water insoluble coupling products. The coupled organic compounds and the copper catalyst are described as being removed by clarification. Since the rate of the coupling reaction was found to be highly dependent on the pH of the water, the process included the addition of lime as a pretreatment step to raise the pH of the water. The pH of the water is later lowered by the addition of acid.

The authors present a cost analysis for their proposed process, along with comparsion analyses for bioxidation and solvent extraction. It should be noted that their cost analysis with regard to solvent extraction contains several conceptual and calculational errors. The solvent extraction analysis includes the addition of a pH adjustment unit, lime treatment unit, calcination unit, and clarifier that are not included in the process analysis from which the authors obtain their solvent extraction cost information. The additional operations are necessary for the removal of phenolics via copper coupling but are not necessary for a solvent extraction process. The design basis chosen by Chin et. al. for comparison is for treatment of a condensate water flow which is 4.12 times larger than that from which they obtained their solvent extraction costs. The installed equipment costs were scaled up from the smaller process to the larger process directly (i.e., multiplying by 4.12) without any benefit of economy of scale. It appears that a more in depth cost analysis is necessary to compare the process.

Klibanov et. al. (1983) have presented an enzymatic coupling approach for removing phenols from coal-conversion wastewaters. Their approach involves the use of horseradish peroxidase and hydrogen peroxide to generate phenoxy radicals, which then react with phenols to produce polyaromatic products. Optimum removal of phenol is reported to be at pH 9. This method when tested on coke plant liquor (pH 8.6) was found to remove 97% phenol at room temperature after one hour.

The extent to which this process would treat solutes other than phenol has not been studied. In addition, the costs associated with the production of the horseradish peroxidase and consumption of hydrogen peroxide would be expected to be large. The potential for recovery of the enzyme was not discussed. The authors suggest that an alternative to the use of horseradish peroxidase would be the development of a microbial counterpart possessing a similar substrate specificity, or to clone the enzyme genes into efficient enyzme-producing microorganisms. This would yield a process that could replace conventional biological degradation, with less sensitivity to pH, temperature, and pollutants. Again, the potential to recover the micoorganism for recycle is a question left unanswered.

I-B-2d. Adsorption

Activated carbon and certain synthetic resins have the advantage of being capable of achieving a very low effluent concentration for adsorbable organics. Depending on the method of regeneration, recovery of the solutes is possible for some adsorbents. The operating costs for an adsorption process are largely dependent on the frequency and totality of regeneration of the adsorbents. Therefore, adsorption is generally limited to the treatment of wastewaters with low solute concentrations, as high solute concentrations would require frequent regenerations. Application of adsorption is limited to higher-molecular-weight solutes, in that low- molecular-weight solutes, such as methanol, have a low activity in water and are not as easily adsorbed.

Ramanathan (1980) presents data for the adsorption of pollutants, including phenol, onto activated carbon and Amberlite XAD-4 (styrene-divinylbenzene copolymer, Rohm and Haas Corp.). Comparisons between the performance of polymeric adsorbents and that of activated carbon for recovering organic materials from wastewater have been discussed by van Vliet and Weber (1981) and Stevens and Kerner (1975). Activated carbons have higher surface areas and generally exhibit larger capacities for organic solutes than synthetic resins. However, regeneration of activated carbons for solutes such as phenol have been accomplished only under extreme conditions (i.e, temperatures above 700 C), resulting in a significant loss in adsorption capacity and poor recovery of the adsorbed organics. Recovery of phenol from activated carbon at lower temperatures (near 250 C) has been shown to yield only a little over 40% recovery of phenol at best (Cha and Glasgow, 1983). The changes occurring during thermal regeneration of the phenol-carbon system have been recently documented by Wang and Smith (1985). Recovery of phenol with synthetic resins has been discussed by Fox (1978) and Kawabata and Ohira (1979), amoung others.

Use of adsorption for condensate water treatment has been discussed mostly as a final treatment step, after bulk removal of organics has been accomplished. Although much work has been done with phenol, little work has been reported on the adsorption of dihydroxybenzenes such as resorcinol. Carbon adsorption has also been found to work synergistically with biological treatment of condensate water when using powdered activated carbon (see for example Yen et. al., 1984). The application of adsorption for treatment of condensate waters is discussed further in Chapter IV.

I-B-2e. Stripping

Removal of dissolved gases such as hydrogen cyanide, hydrogen sulfide, carbon dioxide and ammonia is typically accomplished via stripping. The extent that organic solutes can be recovered from water is governed by the volatility and activity of the solutes in the aqueous phase. Many of the organic solutes in the condensate water have low volatility and are polar in nature (low activity in the aqueous phase), thereby lessening the effectiveness of stripping.

The advantage of stripping is that solutes are recoverable and low effluent levels are achievable. Steam stripping has been shown to be an effective means for the removal of chlorinated hydrocarbons from aqueous streams (Hwang and Farenthold, 1980). Stripping via an inert gas has been used as a method of recovery for residual solvent from aqueous streams for solvent extraction processes (e.g., the Lurgi Phenosolvan Process). In addition, Greminger et. al. (1982) have shown vacuum steam stripping to be an attractive alternative to atmospheric steam stripping for solvent recovery.

The application of stripping with regard to treatment of the condensate waters is discussed further in Chapters III and IV.

I-B-2f. Evaporation

Evaporation has the advantage of being able to concentrate nonvolatile compounds (i.e., salts and heavy organics) in a separate stream of less volume, therby reducing processing cost associated with further treatment. As mentioned above, evaporation has been proposed as part of an incineration process. Low-molecular-weight organic solutes would not be recoverable by this technique. Compounds such as phenol, although higher boiling than water, exhibit a high enough volatility in water to limit the degree of concentration by evaporation. Nevertheless, particularly difficult compounds to remove, such as dihydroxybenzenes, hydantoins and thiocyanate, exhibit extremely low volatilities and could be concentrated to a high degree.

The major drawbacks to the use of evaporation are the large energy consumption for the process and the potential for fouling heat exchange surfaces. Energy costs can be alleviated though the use of multiple effects; however, fouling of heat exchange surfaces would occur rapidly due to the limited solubility of some of the solutes in water. An alternative to direct evaporation may be to perform an equilibrium flash of the condensate. However, an equilibrium flash results in higher losses of solutes in the vapor product for a given liquid/vapor split, and also does not give the energy advantage of multieffect evaporation. The energy requirements for evaporation may be quite low if the condensate is available at a high temperature and pressure. The extent to which some of the compounds distribute in an equilibrium flash has been modeled by Lowell and Noblett (1984).

An alternative related to evaporation would be the use of a two stage condensation process, where the first stage would condense the high-boiling solutes and the second stage would condense the remainder of the condensate water. This option is discussed in more detail in Chapter IV.

I-B-2g. Extraction

The use of solvent extraction for removal of organics from aqueous solutions has recently been reviewed by King and Senetar (1986) Solvent extraction is the basis for the Lurgi Phenosolvan Process, currently in use for condensate water treatment at Sasolsburg, South Africa. Solvent extraction has the advantage that it can be applicable for the recovery of a wide variety of solutes. Depending on the particular system, solvent extraction can also provide selective removal of individual solutes or classes of solutes. The selectivity of solvent extraction for one solute over another has more utility for recovery of expensive chemicals rather than for wastewater treatment.

The disadvantage of solvent extraction is that typical solvents that possess a high enough affinity to extract polar solutes, such as phenol, also have a significant water solubility. This solubility requires further processing to remove and recover the solvent from the aqueous effluent. Solvent recovery is necessary both to reduce the organic level in the treated effluent and to reduce costly solvent losses. Solvent extraction alternatives for the treatment of condensate water are examined further in Chapters III and IV.

I-B-2h. Membrane Processes

Bhattacharyya et. al. (1982) have investigated the use of composite membranes for treatment of coal gasification condensate water. Experiments carried out on selected compounds demonstrated that fairly high retention of phenol (96%) and salts (99%) could be achieved with a high differential pressure (e.g. 2.7 X M Pa) and with the aqueous phase at pH 10 to pH 11. The permeate flux was measured as 5.4×10^{-4} cm^3/cm^2-s. Much lower retention of phenol (77%) was observed for experiments carried out at pH 5 to pH 8.

Membrane processes have the disadvantage of being limited by the large membrane areas necessary in order to handle reasonably large flows. A condensate water flow of 1 MM gal/hr would require at best a surface area of almost 100,000 m^2, based on the above data, if only 50% were taken as permeate. Potential problems with membrane processes are irreversible adsorption of solutes onto the membrane surface, and fouling caused by precipitation of solutes having low water solubility. These difficulties may be overcome to some extent by a pretreatment step such as flocculation; however, this would increase the costs associated with the treatment. More studies are necessary in order to assess the possibilities of overcoming these difficulties.

I-C. Project Goals

I-C-1. Characterization

The analyses presented by Mohr and King (1985)(See Table I-4) demonstrate that between 16% and 30% of the compounds contributing to the chemical oxygen demand (COD) are unidentified. Furthermore, the work of Mohr and King indicates that the unidentified portion of the COD is not easily removed by conventional treatment processes such as solvent extraction with polar organic solvents. Therefore, one major objective of this work has been to identify or sufficiently characterize the compounds that contribute to the unidentified COD, in order to evaluate treatment processes that take advantage of the chemical nature of the unidentified solutes.

Chapter II describes the characterization experiments performed in this work. With few exceptions, the experiments were limited to analysis of a gasification condensate water obtained from the Run-101 of the GFETC Lurgi slagging fixed-bed gasifier, shown in Figure I-2.

I-C-2. Treatment Goals

The goals of the work on condensate treatment have been twofold. One goal has been to use the results of the characterization work to assess the feasibility of current or proposed treatment processes for condensate waters. The other goal has been to investigate alternative treatment schemes that exploit the chemical nature of the solutes. Chapter III presents experimental measurements that were made to assess the effectiveness of various treatment schemes. The results of the experiments presented in Chapter III are then used in Chapter IV to discuss various alternatives for the condensate water treatment.

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CHAPTER II

CHARCTERIZATION OF CONDENSATE WATERS

II-A. Experimental Techniques

II-A-1. Bulk Properties

Bulk properties were measured as a means of accounting for the unidentified compounds in the condensate waters. Properties measured included the chemical oxygen demand (COD), total organic carbon (TOC), organic nitrogen and organic sulfur. Table II-1 compares the theoretical COD and TOC values for three different substances. The COD is a measure of the amount of oxygen required to oxidize a compound to CO_2 and H_2O, and the TOC is a measure of the organic carbon, as carbon dioxide, produced by the oxidation.

The COD was experimentally determined by ASTM Standard Method D1252-78 (ASTM - Water II, 1983), where the material was oxidized with potassium dichromate in the presence of sulfuric acid, using silver sulfate as a catalyst. The method included the addition of mercuric sulfate to decrease the effect of any chloride ions that were present in the sample, up to 1000 mg/L. A spot test for chloride, as described by Luthy (1978), using orthotolodine reagent (orthotolodine dihydrochloride in hydrochloric acid) yielded no response for the presence of chloride in the condensate water samples received; therefore the amount of mercuric sulfate in the COD analyses could have been reduced.

The TOC measurements were determined by vapor-phase oxidation of the sample, using a cobalt catalyst, with subsequent measurement of the

TABLE II-1

COMPARISON OF THE CHEMICAL OXYGEN DEMAND (COD) AND THE TOTAL ORGANIC CARBON (TOC)

Phenol:

$$C_6H_6O + 9/2\ O_2 = 6\ CO_2 + 3\ H_2O$$

Phenol	COD	TOC
1000 mg/L	2380 mg/L	765 mg/L

5,5-Dimethyl Hydantoin (5,5-DHM):

$$C_5H_8N_2O_2 + 9/2\ O_2 = 5\ CO_2 + 2\ NH_3 + H_2O$$

5,5-DMH	COD	TOC
1000 mg/L	1120 mg/L	468 mg/L

Thiocyanate:

$$SCN^- + 2\ O_2 + 2\ H_2O = CO_2 + HSO_4^- + NH_3$$

Thiocyante	COD	TOC
1000 mg/L	1103 mg/L	207 mg/L

carbon dioxide produced by infrared absorption. The TOC measurements were performed by Brown and Caldwell Analytical Laboratory Services (Emeryville, CA).

As demonstrated in Table II-1 the theoretical COD is not necessarily based on the oxidation of nitrogen to molecular nitrogen and sulfur to sulfur dioxide. Mohr and King (1983) determined that the measured COD for 5,5-dimethyl hydantoin corresponded more closely to the conversion of nitrogen to ammonia than conversion of nitrogen to N_2 in the COD determination. The COD of nitrogen-containing heterocycle compounds has been discussed by Chudoba and Dalesicky (1973). In this work, the measured COD of thiocyanate was experimentally determined to be 1.04 mg oxygen per mg thiocyanate, corresponding closely by to that required to convert the sulfur in thiocyanate to sulfate, as illustrated in Table II-1. The measured and theoretical values of the COD for 582 compounds have been presented by Janicke (1983).

Response to the COD analysis is not complete for all compounds. Table II-2 demonstrates the comparison between the measured COD and the theoretical COD for several compounds encountered in this study. The experiments were performed on freshly prepared solutions (approximately 1 g/L) of the solutes. Analytical-grade reagents were used in all cases. The results presented are based on the average of three determinations of each solution. An independent check of the COD determination procedure, using potassium hydrogen phthalate, yielded agreement between the theoretical and experimental values to within 0.5%. A result of the lower-than-theoretical response of the compounds to the COD analysis is an underestimation of the unidentified COD, based on the difference between the measured CO_2 and the total theoretical COD

TABLE II-2

EXPERIMENTAL VERSUS THEORETICAL CHEMICAL OXYGEN DEMAND (COD) FOR INDIVIDUAL COMPOUNDS

Compound	Theoretical COD mg COD/mg Compound	Experimental Results No. of Trials	Experimental Results % Theoretical COD	Experimental Results Standard Deviation
Phenol	2.38	3	99.2 %	0.28 %
Cresols	2.52			
o -		2	94.4 %*	1.2 %
m -		3	99.7 %	0.85 %
p -		2	92.3 %	2.2 %
Xylenols	2.62			
2,6 -		3	96.8 %	0.33 %
3,4 -		3	98.6 %	1.9 %
3,5 -		3	92.8 %	0.28 %

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* Compares to literature value of 95 % (ASTM - Water II, 1983).

of the identified solutes. The difference between the theoretical and measured COD values becomes more important as the unidentified COD becomes less. The COD analyses reported in this work are based on the theoretical COD values, as presented in Appendix A.

In this work, organic nitrogen was defined as the difference between a Kjeldhal nitrogen analysis and an ammonia nitrogen analysis. Both of the analyses are described in Standard Methods (1981) and ASTM Standard Methods - Water I and II (1983). The accuracy of the organic nitrogen determination was increased by first reducing the concentration of ammonia, present in excess in the condensate waters. Ammonia was removed by first adding concentrated sodium hydroxide to raise the sample pH to a value greater than 12, and then stripping with nitrogen (50 L nitrogen/ 10 mL sample). This effectively reduced the ammonia concentration down from >5000 mg/L to approximately 1 mg/L.

Organic sulfur was determined by sample combustion. The gases produced from the combustion of the sample were bubbled through a 3 wt% hydrogen peroxide solution to convert the sulfur dioxide to sulfate for subsequent gravimetric determination of sulfur as barium sulfate. The procedure for the organic sulfur analysis is described by Sundberg and Royer (1948). The term "organic sulfur" is used here to denote any sulfur species that responds to the above analysis and may include both inorganic and organic molecules. Prior to sulfur analysis, the samples were adjusted to pH 2 by the addition of concentrated phosphoric acid and degassed in a Bransonic 220 Ultrasonic Cleaner (Brason Cleaning Equipment) to remove hydrogen sulfide from solution. After degassing, the sample demonstrated a negative test for sulfide, as determined by lead acetate paper. Therefore, the organic sulfur determinations do not include sulfur present as sulfide. Both the sulfur and nitrogen analyses were performed by the College of Chemistry Micro-Analytical Laboratory.

II-A-2. Identification/Quantification

Both gas chromatography (GC) and high performance liquid chromotography (HPLC) were used for the identification and quantification of the compounds in the condensate water samples. HPLC analysis has the advantage over GC analysis in that a variety of reverse-phase columns are available for the direct analysis of compounds in aqueous samples. Also, GC has the major drawback that it is limited to analysis of volatile compounds. GC, particularly capillary GC, performs best when applied to non-aqueous samples. Most of the capillary columns available are incompatible with aqueous-phase analysis, in that water tends to leach off the liquid phase from the capillary, thereby decreasing column efficiency and causing interference for the detection of solutes.

Traditional analytical schemes for GC overcome the problem of working with aqueous samples by first extracting the solutes of interest into an organic solvent (e.g., methylene chloride), and then performing the GC analysis on the extract. This technique is applicable only when the solutes of interest are favorably extracted, such as is the case for many organic solutes that demonstrate high activity coefficients in water. However, some of the identified solutes in the condensate water (i.e., 5,5-dimethyl hydantoin) and some of the unidentified solutes are poorly extracted and therefore are not readily analyzed by this technique. Today, a few bonded-phase capillary columns are available that are applicable for aqueous-phase analysis. Successful aqueous-phase analysis was accomplished in our work using fused-silica capillary columns with bonded-phases, as described below.

GC analysis has the advantage over HPLC analysis in that GC can be easily interfaced directly with a mass spectrometer for identification of solutes, while direct interfacing between HPLC-mass spectrometry (MS) has not been developed to a great extent. There are several instances in the chromatography literature where direct HPLC-MS analysis has been accomplished; however, the application has not been developed to the extent that commercial HPLC-MS systems are available. Although GC-MS analysis is in wide use, the application favors non-aqueous samples over aqueous samples due to both the lack of columns compatible with water and the persistence of water in the mass spectometer, leading to interference.

II-A-2a. Gas Chromatography

Both packed and capillary GC columns were employed for the analyses in this work. Gas chromatographic separations were first performed in the laboratory using a Model 3700 Gas Chromatograph (Varian Associates) equipped with a flash injector and a flame-ionization detector. Later, identification of the eluted compounds was performed by the College of Chemistry Mass Spectrometry (MS) Laboratory, using the same capillary columns as in the laboratory analysis at the predetermined conditions for the separation.

Acetone, acetic acid, and methanol were measured from direct analysis of the aqueous sample on a 1-ft Porapak-Q (100-120 mesh, Waters Associates) column, fabricated from 1/8 inch o.d. stainless steel tubing

(26 gauge). The low-molecular-weight compounds were eluted isothermally at 70 C, followed by a temperature program of 20 C/min, up to 240 C, to remove the less volatile solutes from the column. The temperature was held at 240 C for 5 minutes before resetting back to the initial temperature. The chromatogram for the analysis is presented in Appendix II-B.

Two different capillary columns were investigated for the direct analysis of the condensate waters, a DB-17 column and a DB-Wax column (both from J&W Scientific). Both columns were 30 meters in length, 0.25 mm inside diameter, with a film thickness of 0.25 microns. The DB-17 column had a methylphenyl-polysiloxane film (50% methyl - 50% phenyl) bonded to a fused-silica capilllary. The DB-Wax capillary column employed a polyethylene glycol phase bonded to a fused-silica capillary. Both columns were operated with a temperature program from 60 C, at injection, to 250 C final temperature, at a rate of 2 C/min. Helium was used as the carrier gas. The DB-Wax column was reported to degrade rapidly at high temperature in presence of oxygen (J & W Scientific, 1983). High purity helium and a Gas Purifier (Varian Associates, cat. no. 68-00056-01) were installed to reduce the oxygen level to below 1 ppm to avoid column damage. Appendix B presents the chromatograms obtained for the aqueous phase analysis of the METC Run-101 condensate water using the two columns.

II-A-2b. High Performance Liquid Chromatography (HPLC)

HPLC analyses were performed using a Model SP8000 Liquid Chromatograph (Specta-Physics) for flow control and an RCM-100 Radial Compression Module with Radial Compression Cartridges (both from Waters

Associates) for separation. Detection of compounds was accomplished using a Model LC-75 Variable Wavelength Spectophotometric Dectector (Perkin Elmer Corp.) operating in the ultra-violet range. A Model 2211 SuperRac fraction collector (LKB-Produkter AB) was interfaced with the detector and operated in peak detection mode.

HPLC analysis using a C_{18} μ-Bondapak column provided the primary method for analysis of the condensate waters. Detection of the compounds was made at 192 nm. A pH-3 phoshate buffer was used to surpress the ionization of the acidic solutes during analysis. The pH-3 buffer was prepared by diluting 20 mL of buffer concentrate (108.8g KH_2PO_4 and 22.6 mL conc. H_3PO_4 per liter) to 4 L with purified distilled water. The purified, distilled water was obtained from treating distilled water with a Milli-Q Water Purification System (Milliipore Corporation), containing a carbon adsorption and 2 ion exchange cartridges. Water treated by this method is commonly called Milli-Q grade water. Hydroquinone, resorcinol, and 5,5 dimethyl hydantoin were separated by isocratic analysis using a mobile phase of pH-3 phosphate buffer, at a flow rate of 1 mL/min. The mobile phase was filtered through a Millipore Type HA 0.45-μm filter (Millipore Corporation) before use.

Quantification of catechol, 4-methyl catechol, hydroxybenzenes, and naphthols was performed using the C_{18} μBondapak column with gradient elution at 1 mL/min of 100% pH-3 buffer, from injection until 6 min had elapsed, followed by a linear gradient to 100% methanol, attained 46 minutes after injection. The gradient was held at 100% methanol until all compounds had eluted from the column. The total analysis time was about 55 minutes, depending on the column condition. The 6 minute lag time was a result of a hold-up volume of approximately 6 mL between the solvent switching valve and the injection valve. HPLC-grade methanol (Burdick and Jackson Co.) was used in the analysis. The methanol was filtered through a Millipore Type FH 0.25-μm filter (Millipore Corporation) prior to use.

Samples were prepared for both the isocratic and gradient analyses using Sep-Pak C_{18}-Cartridges (Waters Associates) to adsorb any material that would irreversibly adsorb on the C_{18}-column. First, the sample was pipetted into a syringe, passed through the Sep-Pak cartridge, and collected. Next, an equal volume of aqueous mobile phase (pH 3 buffer) was pipetted into the syringe and collected along with the eluted sample. The procedure was repeated with methanol to yield a sample of one-third concentration. The Sep-Pak cartridge was washed with methanol before use to wet the surfaces of the particles in the cartridge, so as to promote adsorption. All samples were filtered through a Millex-SR 0.5 μm filter unit (Millipore Corporation) before injection. Chromatograms for both the gradient and isocratic analyses of the METC Run-101 condensate water can be found in Appendix C.

In addition to the analyses described above, the condensate water was analyzed by both isocratic and gradient elution using a 0.01 M di-(n- butyl amine) phosphate solution in place of the pH-3 buffer for the analysis and sample preparation. The mobile phase was prepared using 10 mL D-4 Modifier (Waters Associates) diluted to 1 liter. Use of the D-4 Modifier permits the separation of weak-base compounds, such as amines, on a C_{18}-column at low pH. No unidentified peaks were observed when the analysis was performed on the condensate water, indicating no appreciable concentration of amines present in the condensate water.

An IC-Pak A (Waters Associates) anion-exchange column was investigated to perform a separation of the solutes that eluted quickly on the C_{18}-column. The IC-Pak A column was stable at both high pH and low pH, allowing a variety of buffers to be investigated for the mobile phase. The goal of the separation was to collect fractions containing the separated components and then submit the fractions for MS analysis. A dilute sodium bicarbonate solution (0.001 M) in 10 % acetonitrile was found to yield a favorable separation and to give minimal interference with the MS analysis. The dilute sodium bicarbonate solution was favored over a pH buffer of higher ionic strength since the dilute sodium bicarbonate solution yielded a lesser interference for the MS analysis. The column was limited to a maximum of 10 vol% organic solvent in the mobile phase. This method confirmed the presence of thiocyanate in the condensate water.

II-A-2c. Mass Spectometry (MS)

In this work low-resolution mass spectometry was performed using a Finnigan 4000 mass spectrometer, operating in both electron ionization (EI) and chemical ionization (CI) modes. Low-resolution MS was employed for both the GC-MS analyses and for the MS-probe analyses. High-resolution MS, using a Kratos MS-50 mass spectrometer, was also employed for MS-probe analyses. The results are discussed in Section II-B-2.

II-A-2d. Thiocyanate Analysis

Thiocyanate was determined by an adaptation of the technique presented in Standard Methods (1981). A 10 mL sample of the condensate water (diluted to contain less than 50 mg/L thiocyanate) was adjusted to pH 3.0 - 3.5 by the addition of 1+1 nitric acid (50 vol% concentrated nitric acid - 50 vol% water), and placed in a 60-mL separatory funnel. A A 5-mL aliquot of copper solution (containing 1 g/L Cu^{++} in nitric acid) and 1 mL of pyridine were added to the separatory funnel to produce a deep blue solution containing a coppper(II)-pyridine-thiocyanate complex. The complex was extracted into 10 mL chloroform to yield a light-green extract. The absorbance of the extract at 450 nm was measured using a Spectronic 710 Spectrophotometer (equipped with a flow cell) interfaced with a Spectronic System 400 auto sampler and DP 110 data processor (all supplied by Bausch & Lomb). The absorbances of the samples were compared with the aborbances of the extracts obtained by analyzing standard solutions (0, 11, 22, 33, 44, 55 ppm thiocyanate as KSCN) to obtain the concentration of thiocyanate in the sample. The absorbance was found to be linear for samples containing between 22 ppm and 55 ppm thiocyanate. The 0-ppm standard was used to zero the spectrophotometer at the start of the analysis. When the analysis on the condensate water was performed, a chloroform extract of the condensate water without the reagents was analyzed to obtain the background interference resulting from substances in the condensate water. The background interference was small in comparison to the total adsorbance of the sample. The results obtained for the condensate water were corrected for this background.

The method presented in Standard Methods (1981) uses the measured absorbance at 407 nm, rather than at 450 nm. In this work, analysis at 407 nm was attempted; however, the results were irreproducible. Chloroform was found to have a relatively large absorbance at 407 nm, which rapidly decreased with a small increase in wavelength. At 450 nm, the chloroform had a low absorbance which changed little with wavelength; therefore, results at 450 nm were more reproducible than at 407 nm. The response of the thiocyanate complex at 450 nm was found to be one-third of that measured at 407 nm. Nevertheless, accurate and reproducible results were still obtainable at 450 nm for solutions containing greater than 11 ppm thiocyanate.

Preparation of the copper solution used in the analysis differed from that described in Standard Methods. In this work, the copper solution was prepared by dissolving 2.9 g copper(II) nitrate in water, adjusting to pH 3.0 - 3.5 with 1+1 nitric acid, and diluting to 1 liter. The method described in Standard Methods calls for dissolving 1 g copper wire in nitric acid, diluting to 900 mL, raising to pH 3.0 - 3.5 with sodium hydroxide, and then diluting to 1 L. Copper(II) nitrate was chosen to produce a solution similar to that in Standard Methods; however, a copper (II) sulfate solution, such as that used by Kruse and Mellon (1953), could also have been used.

II-A-2e. Polysulfide Analysis

Polysulfide (S_xS^{2-}) is a combination of one or more sulfur atoms in the zero oxidation state with a sulfide ion (S^{2-}) to form an ion with a formal charge of -2. Krachner (1970) reports that polysulfides up to hexasulfide (S_5S^{2-}) have been shown to exist. The analysis of polysulfide sulfur was performed by conversion of the S_x to thiocyanate followed by subsequent determination of the increase in thiocyanate concentration in the sample. The sulfide ion does not respond to the test. Thiocyanate concentration was determined as described above in Section III-A-2d.

The procedure used for converting S_x to thiocyanate was that described by Krachner (1970). First, 50 mL of 20 g/L boric acid was placed in a 300 mL three-neck round bottom flask fitted with a condenser. The two side arms were stoppered and used to add the reagents into the flask. A heating mantle was attached to the flask and the contents were boiled for 2 minutes to expel air. Next, 1 mL of 10 wt% potassium cyanide solution and 10 mL of the condensate water were pipetted into the flask and the contents were boiled for an additional 10 minutes. The heating mantle was removed and the contents were left to cool before initiating the thiocyanate analysis. A thiocyanate analysis was performed on both the reaction solution and a sample of the condensate water. The amount of S_x was calculated from the difference in thiocyanate concentration between the reacted sample and the condensate water, accounting for dilution. A one-to-one stoichiometry exists between each mole of thiocyanate formed and each mole of S_x in the original sample.

The above procedure requires that the pH of the reaction solution be maintained below pH 7. The condensate water was adjusted to below pH 7 by the addition of concentrated phosphoric acid before analysis to ensure that the pH would remain below pH 7 after the addition of the condensate water. Both HCN and H_2S are evolved from the reaction solution during the analysis; therefore, the procedure must be performed in a adequately vented fume hood. As an additional precaution against exposure to HCN, the condenser was vented into the fume hood with plastic tubing.

II-A-2f. Amino Acid Analysis

The condensate waters were analyzed for the presence of amino acids by a procedure similar to that described by Hogan et al. (1982). In this method, primary amino acids are derivatized with o-phthaldialdehyde (OPA), separated by HPLC, and measured by fluorescence. First, 0.5 mL of derivatization solution was added to a 0.5 mL aliquot of sample and mixed virgorously for 40 seconds using a Model K-500-4 Vortex Tube Mixer (Scientific Industries) at high speed. The derivatization solution was prepared from 50 mg OPA , 1.25 mL methanol, 50 µL 2-mercaptoethanol, and 11.2 mL of 0.4 M sodium borate to yield a pH 9.5 solution. The solution was purged with nitrogen and then stored in an amber bottle for 24 hours before use.

After 60 seconds had elapsed since the solutions were first contacted, the sample was injected into the HPLC and separated isocraticly on a C_{18}-column using a pH 3 phosphate buffer (as described above in Section II-A-2b). The fluorescent derivatives were measured with a Kratos FS 970 fluorometer (Spectros Inc.) operating with excitation at 330 nm and measurement of fluorescence at 460 nm.

At first, derivatization of the excess ammonia present in the sample led to a large peak that interfered with the analysis. The sample was stripped at high pH with nitrogen (as described above for the nitrogen analysis) to remove the interference of ammonia. After stripping, no peak was observed, indicating that no primary amino acids were present in the condensate water.

Other methods of amino acid analysis were investigated prior to the amino acid analysis described above. Both the ninhydrin procedure (Milton, 1955) and the preparation of 3,5-dinitrobenzoates of amino acids (Cheronis and Entrinkin, 1947) led to inconclusive results, due to interferences from the organics in the solution. This led to the method outlined above which provided separation of the amino acid from the other organic compounds.

II-A-3. Additional Apparatus

In addition to the analytical instuments described above, several other pieces of apparatus were used for the experimental determinations in this work. To prevent oxidation of samples, some experiments were performed in a glove box blanketed with a nitogen atmosphere. A VWR 1410 Vacuum Drying Oven (VWR Scientific) was employed for drying adsorbents and evaporating mixtures. Water used for all the experiments was obtained from a Milli-Q Water Purification System (Millipore Corporation), operating with a distilled water feed. Measurement of pH was performed using a Model 701 A digital Ionalyzer employing a Model 81-02 Ross pH electrode (both from Orion Research).

Contacting of phases for batch extraction and batch adsorption experiments was accomplished using a Model 50 Presicion Shaking Water Bath (GCA Corporation) operating at 30 C and 100 excursions per minute, unless otherwise noted. Phase separation was performed with an IEC HN-SII Centrifuge (International Equipment Corporation) at 2500 rpm.

Ultrafiltration experiments were performed using an Amicon Model 12 ultrafiltration apparatus (Amicon Corporation). The apparatus used 25-mm Diaflo Ultrafiltration Membranes (Amicon Corporation), and stirring was accomplished via a magnetic stirring bar and driven by an external magnetic stirrer, suspended above the membrane. Flow through the membrane was driven by 90-psig pressure of nitrogen.

II-B. Characterization Results

II-B-1. Isolation and Concentration Experiments

Phenolic compounds, such as phenol, cresols, and xylenols, comprise the majority of the organic solutes in the condensate water. The major phenolic compounds in the condensate water were found to interfere with GC-MS identification of the other solutes in the condensate water. Various means were used to isolate the unidentified solutes in the condensate water from the bulk of the identified solutes, while at the same time concentrating the unidentified solutes so as to provide greater ease of identification. Discussed below are the techniques that were used in the isolation and concentration of the unidentified solutes in the condensate water.

II-B-1a. Isopropanol Substitution

Mohr and King (1985) describe the technique whereby 5,5-dimethyl hydantoin was identified in a coal-gasification condensate water. In this procedure, an aqueous fraction (5 mL) containing the hydantoin was combined with an excess of isopropanol (50 mL), and then reduced to a small volume (1 mL) by evaporation. The evaporated sample was then recombined with an excess of isopropanol (10 mL) and reduced again in volume (0.1 mL). The final sample, now containing little water, was then submitted for GC-MS analysis. This method can effectively produce a non-aqueous sample for capillary GC and/or GC-MS, provided that the solutes are nonvolatile enough not to be lost in the evaporation step, and volatile enough to go through a capillary GC column. Solutes that are extremely nonvolatile can be analyzed by MS-probe analysis; however, separation from other solutes must be accomplished beforehand.

In this work, the isopropanol substitution procedure was applied to the complete condensate-water sample. The resulting non-aqueous sample was analyzed for water and found to contain less than 1 wt% water. The non-aqueous sample was submitted for GC-MS analysis; however, the analysis did not yield any new results. This in part was due to the large excess of phenolic compounds that interferred with the analysis. Other methods were then explored to isolate the unidentified compounds from the abundant phenolics.

II-B-1b. Ultrafiltration

Table II-3 presents results obtained by ultrafiltration of METC Run-101 condensate water, using an Amicon UM-2 membrane (1000 molecular weight cutoff). The experiments were carried out using three condensate water samples, the as-received, unacidfied (pH 8.5) sample, the as-received, acidified (pH 2) sample, and the as-received, unacidified condensate sample that was acidified to pH 2, with phosphoric acid, prior to use. The data show that in all three experiments the permeate has a lesser COD than the retentate. This indicates that solutes of higher molecular weight may be present in the condensate water. In all cases less than 100% of the original COD was accounted for between the permeate and the retentate. The missing COD was most likely present on the membrane at the end of a run. The lesser percentage recovery of COD for the samples stored at high pH, regardless of the pH when filtered, indicates that the higher-molecular-weight compounds may form during aging at high pH.

TABLE II-3

ULTRAFILTRATION OF METC RUN-101 CONDENSATE WATER*

Membrane: Amicon UM2 (1000 MS Nominal Cutoff)

Sample	(Sample COD / Condensate COD) x 100 Retentate	Permeate	% COD Recovered	Permeate Volume / Total Sample Volume
Received Acidified	118.	76.2	90.8 %	62 %
Non-Acidified	87.5	59.2	75.9 %	17. %
Re-Acidified	82.5	53.1	72.4 %	50. %

---

* All samples were passed through a 0.5 μM filter before being introduced into the ultrafiltration cell.

II-B-1c. Extraction

Extraction was used both as a means of determining the chemical behavior of the unidentified solutes and as a means of sample preparation for GC-MS analysis. Presented in Table II-4 is the measured extractability of organic sulfur from the METC Run-101 condensate water, into methylene chloride and MIBK at both high and low pH. These results were obtained from batch extractions at 30 C with a solvent-to-water ratio of 1.0, by volume. The measured pH of the METC Run-101 condensate water received was 8.5. The low pH extractions were performed on non-acidified condensate water that was adjusted to low pH, with concentrated phosphoric acid, just prior to use. The extractions and pH adjustment were performed under a nitrogen atmosphere.

The results in Table II-4 demonstrate that the organic sulfur is extracted better at pH 8.5 than at pH 2, into both solvents, indicating that the sulfur-containing species could have been at least partially ionized at the low pH. Ionization at low pH is characteristic of a weak base molecule However, the fact that the organic sulfur was extracted more by methyl isobutyl ketone (MIBK, a Lewis base) than by methylene chloride (a Lewis acid), suggests that the organic sulfur compounds extracted had more Lewis-acid character than Lewis-base character. Later experiments demonstrated that the organic sulfur measurements were due to the presence of thiocyanate and polysulfide ions in the condensate water, both of which should be ionized at the higher pH. Therefore, it appears that these sulfur containing compounds are more easily extracted as ion- pairs than in their dissociated forms.

As previously mentioned, extraction of an aqueous sample with a water immicible solvent can produce a non-aqueous sample suitable for

TABLE II-4

EXTRACTION OF ORGANIC SULFUR FROM METC RUN-101 CONDENSATE WATER INTO METHYL ISOBUTYL KETONE AND METHYLENE CHLORIDE AT pH 2 AND pH 8.5

	% Organic Sulfur Extracted	
	pH 2	pH 8.5
Methylene Chloride	0 %	24 %
Methyl Isobutyl Ketone	3 %	57 %

---

* Batch extracted at 30 C with a solvent-to-water ratio of 1.0, by volume.

GC-MS analysis. A portion of the nonacidified METC Run 101 condensate water was extracted with methylene chloride at a solvent-to-water ratio of 1.0 at room temperature, and submitted for GC-MS analysis. As was the case with conversion to an isopropanol solution, this method did not reveal any unidentified compounds and was hindered by the presence of large amounts of phenolic compounds. The method was repeated, this time performing two extractions in sucession. The first extract contained the bulk of the phenolics, while the second extract contained a much diminished amount of phenolic compounds. The second extract was then submitted for GC-MS analysis. Although this method was successful in producing a suitable nonaqueous sample with diminished phenolic compounds, the concentrations of unidentified compounds were too low for precise MS analysis. The extract from the second extraction was reduced in volume by vacuum evaporation to concentrate the solutes; however, still no precise GC-MS results were obtainable. It became apparent that either the compounds of interest were not extracted to any great extent by methylene chloride, or they were extracted to a great extent in the first extract, but could not be analyzed due to the presence of the phenolics.

Mohr and King (1983) give results for the extraction of COD from a condensate water with methylene chloride and methyl isobutyl ketone (MIBK). Their results demonstrate that methylene chloride extracts the COD to a lesser extent than MIBK. Using this information, the METC Run-101 condensate water was extracted again, first with methylene chloride, and second by MIBK. The MIBK extract was submitted for GC-MS analysis; however, no new information was obtained.

II-B-1d. Adsorption / pH Fractionation

i. XAD-4 Resin

Presented in Table II-5 are the results of a fractionation of the METC Run-101 condensate water based on selective adsorption of solutes onto Amberlite XAD-4 resin (styrene-divinylbenzene copolymer, Rohm and Haas Corp.) at low pH, with subsequent elution of the solutes with buffer solutions of successively higher pH. The results in Table II-5 were obtained by using a 20-cc bed of XAD-4 resin (20 - 50 mesh) packed in a 25-mL buret. A 10-mL portion of the condensate water was adjusted to pH-3, by the addition of concentrated phosphoric acid, and passed through the column and collected. A 20-mL portion of the pH-3 buffer solution was then passed through the column and collected along with the first 10-mL eluted, to make up the pH-3 sample. Next, 30-mL each of pH-7 buffer and pH-10 buffer were passed through the column sucessively to yield the pH-7 and pH-10 samples, respectively.

The resin was washed extensively prior to use. The resin was first placed in a Buchner funnel and washed with methanol (100 mL methanol/20 cc resin) and placed overnight in a vacuum drying oven at 70 C and approximately 5 inches Hg. The vacuum drying oven was operated with a slight air purge to speed the drying process. After drying, the resin was slurried with a 10 vol % methanol in water solution, and poured into the buret. Water alone would not wet the surface of the dried resin; therefore, methanol was added in order to allow the resin surface to wet. Before use, the resin was rinsed with 6 liters of water to remove the methanol from the bed. A COD measurement on the wash water demonstrated no appreciable level of COD (< 10 mg/L).

TABLE II-5

pH FRACTIONATION OF METC RUN-101 CONDENSATE WATER WITH XAD-4 RESIN

Compounds	COD in Fractions Collected (mg/L) pH 3	pH 7	pH 10	COD METC Run-101
Phenol	<25.	<25.	<25.	3,290.
Cresol	<25.	<25.	<25.	5,000.
Xylenol	<25.	<25.	<25.	2,210.
Catechol	<24.6	0.	0.	81.
Resorcinol	<67.5	33.8	0.	125.
Hydroquinone	6.4	0.	0.	8.
4-Methyl Catechol	0.	0.	0.	80.
5,5-Dimethyl Hydantoin	123.2	37.9	0.	108.
Calculated COD for above compunds	<311.	<151	<75.	11,038.
Measured COD	1,489.	788.	652.	12,520.
Unidentified COD	>1,178.	>637	>577	1,482.
Organic S (mg/L)	347.	20.	6.7	404.
Organic N (mg/L)	113.	13.	53.	140.

The fractionation described above is a form of displacement-development chromatography (King, 1980), where acidic compounds should elute in the pH fraction that has a pH greater than the pK_a of the compound. The data in Table II-5 illustrate that this method was effective in isolating the compounds contributing to COD, organic nitrogen, and organic sulfur away from the bulk of the phenolic compounds. The sum of the unidentified COD for the fractions exceeds that of the original sample due in part to the errors in volume measurement but also due to the displacement of organics from the resin. Nevertheless, the results indicate that the bulk of the unidentified COD, organic nitrogen, and organic sulfur elute in the first (pH 3) fraction. The results were an indication that the unidentified COD might be attributed to the presence of organic-nitrogen and organic-sulfur containing compounds.

ii. Dowex 50W-X Cation-Exchange Resin

The pH-fractionation procedure described was repeated using Dowex 50W-X resin (Dow Chemical) substituted for Amberlite XAD-4; however, the resin in this case was washed with water only and not dried afterward. The results are presented in Table II-6. Dowex 50W-X resin is a strong-acid cation-exchange resin with sulfonic acid groups. The resin used was 20 - 50 mesh and in the hydrogen form.

Under the conditions of this experiment, the compounds should be separated by increasing basicity, where a compound with higher pK_b should elute in the higher pH fraction. Table II-6 demonstrates that a small portion of the unidentified COD elutes in the low pH fraction, while the majority of the unidentified COD remained on the column. This

TABLE II-6

pH FRACTIONATION OF METC RUN-101 CONDENSATE WATER WITH DOWEX 50W-X RESIN

	Calculated COD in Fractions Collected (mg/l)			
Compounds	pH 3	pH 7	pH 10	METC Run-101
Phenol	157	1071	904	3,290
Cresol	101	630	630	5,000
Xylenol	0	115	131	2210
Catechol	0	0	0	81
Resorcinol	27	113	34	125
Hydroquinone	0	0	0	8
4-Methyl Catechol	0	0	0	80
5,5-Dimethyl Hydantoin	0	0	0	108
Calculated COD	285	1,929	1,729	11,040
Measured COD	670	1,880	1,720	12,520
Unidentified COD	385	-49	-9	1,480

---

* COD values are corrected to the original volume of the condensate water sample.

indicates that the bulk of the unidentified COD appears to be protonated at low pH. The data presented here for the Dowex 50W-X resin and that presented above for the Amberlite XAD-4 resin are in agreement with the previously reported extraction data that demonstrated the inability of organic sulfur compounds to be extracted at low pH. If the COD and organic sulfur are attributed to the presence of thiocyanate and/or polysulfide, it appears that at least one of the two species is able to be removed as an ion-pair, even at low pH.

iii. AG 1- X8 Anion-Exchange Resin

The affinity of solutes for an anion-exchange column was studied using an AG 1-X8 Econo-Column (quaternary ammonium resin, Bio-Rad Laboratories). The results of the experiment are summarized in Tables II-7a and II-7b. The column contained 2 cc of 100 - 200 mesh resin in the chloride form. In this experiment, a 10 mL portion of condensate water, previously extracted with MIBK (S/W = 1.0 by volume), was first passed through a 20 cc bed of Amberlite XAD-4 resin, collected, and then passed through an AG 1-X8 Econo-Column. The results in Table II-7a demonstrate that the Amberlite XAD-4 resin removed about half of the remaining COD in the condensate water, some of which is most likely residual solvent; however, removal of the organic nitrogen and organic sulfur compounds was small. On the other hand, the anion-exchange column greatly reduced the COD, organic nitrogen, and organic sulfur of the XAD-4 eluent. Table II-7b presents balances for COD, organic nitrogen, and organic sulfur around the anion exchange column. Included in Table II-7a is the experimental response, as a fraction of the theoretical response, of thiocyanate for the nitrogen and sulfur

TABLE II-7a

CHEMICAL OXYGEN DEMAND (COD), ORGANIC NITROGEN, AND ORGANIC SULFUR REMOVAL BY RESINS

Sample	COD	Concentrations (mg/L) Organic N	Organic S
METC Run-101 Condensate Extracted and Stripped	1730	156	528
XAD-4 Eluent	820	102	414
Anion-Exchange Eluent	102	16	172

TABLE II-7b

CHEMICAL OXYGEN DEMAND (COD), ORGANIC NITROGEN, AND ORGANIC SULFUR BALANCE AROUND THE ANION-EXCHANGE COLUMN

	mg/L XAD-4 Eluent	Anion Eluent	Diff.	SCN^- Response*	Corrected Diff. (mmol/L)
Organic Nitrogen	102	16	86	0.755	8.1
Organic Sulfur	414	172	242	0.929	8.1
COD	820	102	718	----	11.2**

---

* These values reflect the less than theoretical response of thiocyanate to the organic sulfur and organic nitrogen measurements.

** The amount of thiocyanate which would have been present if all the adsorbed COD were attributed to thiocyante.

analyses. Assuming the removed specie is thiocyanate, the results indicate that a 1:1 stoichiometric ratio of organic nitrogen and organic sulfur was observed to have been removed from the condensate water by the anion column. This result strongly indicates thiocyanate as the principal substance removed by the anion-exchange column.

Significant amounts of organic sulfur and COD are not removed by the anion column, suggesting that the remaining COD has to be attributable to other organic-sulfur compounds.

II-B-1e. Distillation

A batch distillation was performed on the condensate water in order to assess the volatility of the organic-sulfur containing compounds. This experiment was performed on a condensate-water sample obtained from Run-106 of the gasifier at the Grand Forks Energy Technology Center (GFETC) in North Dakota. A 100-mL sample of the condensate water was placed in a 250-mL round-bottom flask and distilled under a house vacuum. Two successive distillate fractions were obtained, corresponding to 27 vol% and 46 vol% of the original solution, respectively. The two distillate samples were found to contain only 1% and 2%, respectively, of the total organic sulfur in the original sample. The remaining 97% of the organic sulfur remained in the bottoms product (27 vol%). Mohr and King (1983) present similar results for the volatility of organic nitrogen compounds in a different sample of GFETC condensate water. The lack of volatility for both the organic sulfur and organic nitrogen compounds led to using evaporation as a technique for concentrating and isolating these compounds.

II-B-1f. Evaporation

Table II-8 presents the distribution of compounds in the METC Run-101 condensate water, as obtained by evaporation. A 250-mL sample of condensate water was introduced to a 500-mL round-bottom flask and attached to a rotary evaporation apparatus. A vacuum was drawn on the sample, and the the flask was then placed in a temperature bath at 50 C. The vacuum pump used was capable of achieving a vacuum of 20 μm Hg absolute. A liquid nitrogen trap was placed between the flask and the pump to collect the evaporated liquid. The evaporation was stopped when all the liquid had evaporated and only solids remained in the flask. The solid product was redissolved in water to bring the volume up to the original volume of the sample. Both the samples were analyzed for the COD, organic nitrogen, and organic sulfur, as well as a component analysis by HPLC.

The results demonstrate that the unidentified COD, organic nitrogen, and organic sulfur primarily remained in the solids left after evaporation. The unidentified portion of the COD in the condensed product can be attributed to low-molecular-weight organic compounds that were not determined in this analysis. This method successfully obtained the unidentified solutes in a concentrated form that was isolated from the bulk of the phenolic compounds. The evaporation experiment was repeated, this time with an attempt to dissolve the solids in 25 mL of methylene chloride rather than 250 mL of water. Not all of the solids were soluble in methylene chloride. The methylene chloride phase was submitted for GC-MS analysis. The results confirmed the presence of 1-naphthalenol (1-naphthol) and 2-naphthalenol (2-naphthol) in the

TABLE II-8

DISTRIBUTION OF COMPOUNDS BY EVAPORATION

	Concentration of Solutes (mg/L)		
Compounds	Redissolved Solids	Condensed Product	METC Run-101 Condensate
Hydroquinone	4.3	0.	0.
Resorcinol	64.2	0.	61.6
Catechol	51.2	0.	40.5
4-Methyl Catechol	38.6	0.	40.5
Phenol	30.8	1,256.	1,220.
Cresol	17.4	1,544.	1,508.
Xylenol	55.6	1,262.	1,260.
5,5 Dimethyl Hydantoin	112.	0.	108.
Calculated COD	593.	10,190.	10,000.
Measured COD	2,100.	10,530.	12,250
Unidentified COD	1,517.	340.	2,250
Organic N (mg/L)	173.	0.	140.
Organic S (mg/L)	404.	0.	404.

condensate water. The amount of the naphthols present in the condensate water was determined by HPLC as described in Section II-A-2a.

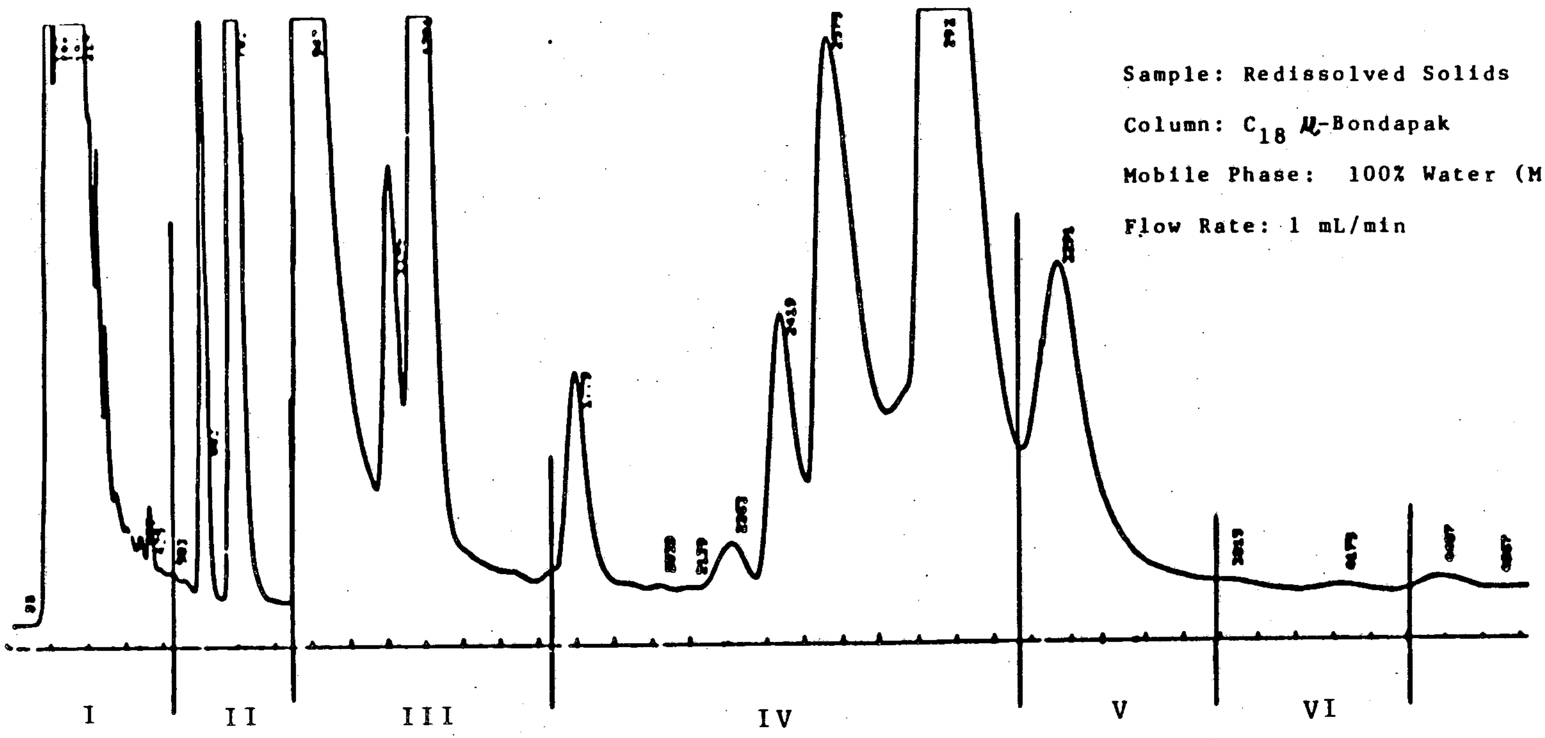
II-B-1g. HPLC Fractionation

An HPLC analysis was performed on the redissolved solids (as obtained above in Section II-B-1f) using a C_{18} μ-Bondapak (Waters Associates) column with a 1 mL/min flow rate of Milli-Q grade water as the mobile phase. The sample was prepared for analysis using the Sep-Pak procedure outlined in Section II-A-2b, only in this case the methanol rinse of the Sep-Pak was omitted. Detection was made with the UV-detector operating at a 192 nm wavelength. The effluent from the detector was fractionated through the use of the Super-Rak 2211 fraction collector. The parameters used for the fraction collection are presented in Appendix D. Individual peak fractions were combined as necessary to permit furthur analysis of the effluent. Figure II-1 presents the chromatogram for this separation, along with the COD analyses of the combined samples.

The results in Figure II-1 demonstrate that a large portion of the unidentified COD elutes in the first fraction of the effluent. The values for the unidentified COD for the fractions contain a large uncertainty, as evidenced by the negative unidentified COD in fraction II. This resulted from an unstable COD measurement for the background which may be attributed to column bleed. The measured COD values reported in Figure II-1 have been corrected for an average COD of the column effluent prior to injection. Also, as is the case with Fraction II, the uncertainty in the COD analyses is larger for the more dilute samples. Nevertheless, the results of the fractionation indicated that

FIGURE II-1

HPLC ANALYSIS OF REDISSOLVED SOLIDS FROM METC RUN-101 CONDENSATE WATER



Sample: Redissolved Solids

Column: C_{18} μ-Bondapak

Mobile Phase: 100% Water (Milli-Q Grade)

Flow Rate: 1 mL/min

Chemical Oxygen Demand (mg/L)

Fraction	I	II	III	IV V VI	Total
Measured:	783	4	206	933	1986
Identified:	0	180	187	345	712
Unidentified:	783	-176	19	648	1274

a significant fraction of the unidentifed COD was eluting in the first fraction, and that this method of fractionation was able to separate unidentified solutes from the identified solutes.

The Sep-Pak was used for sample pretreatment to enable any solutes that would irreversibly adsorb onto a C_{18}-column to be removed from the sample prior to analysis. The extent that the Sep-Pak altered the COD of the sample was examined, and it was found to have a small effect. A sample of the redissolved solids (COD of 1910 mg/L) was treated with the Sep-Pak, and the effluent was found to have a COD of 2100 mg/L. The measured COD of the sample with no treatment also compared well with the COD for the HPLC fractions.

The fractionation was repeated, and the first fraction was prepared for MS-probe analysis. Preparation involved reducing the volume of the sample from approximately 10 mL to 0.1 mL by vacuum stripping the sample with air. The 0.1 mL sample was divided amoung several glass capillary tubes, and then placed in the vacuum drying oven at 60 C overnight to evaporate it to near dryness. A low resolution MS analysis of the sample was confounded by the presence of alkyl silane compounds in the column effluent. Leaching of material from silica-based columns, such as the C_{18}-column used in this experiment, has been reported by Waters (1983) to be a strong function of the pH of the mobile phase. The leaching of silane increases at higher pH, with a very rapid increase in silane losses occuring above pH 8. When the fractionation was repeated using a mobile phase of pH-3 phosphate buffer (see Section II-A-2b for buffer composition), the presence of silane compounds was greatly decreased; however, the presence of the phosphate buffer greatly interferred with the MS analysis. Further experiments demonstrated that a 0.01 N solution of HCl used as the mobile phase inhibited the leaching of silane and was effectively removed from the sample in the evaporation step. An MS analysis of the sample obtained using HCl identified thiocyanate as the major component in the large peak that eluted first in the chromatogram. The MS results are presented in Appendix II-E.

II-B-2. Results of Characterization

Table II-9 and Table II-10 present a summary of the compounds that were identified as being present in the METC Run-101 condensate water. Table II-9 indicates the methods used for confirming the presence of the compounds and the methods used to determine the concentration of the solutes in the condensate water. Table II-10 presents the concentrations of these solutes found in the METC Run-101 condensate water, as well as the contributions of the compounds to the COD and TOC of the sample. Compounds designated with an asterik (*) in Tables II-9 and II-10 are ones that were not found in the analyses reported by Mohr and King (1983). Also, the numbers appearing in brackets are reported for a nonacidified sample that has aged and were found to change with time.

The naphthols were found to be present in the condensate water through the use of the evaporation procedure described in Section II-B-1f. The presence of the naphthols was confirmed by low-resolution GC-MS (EI mode) and co-chromatography in both GC and HPLC analyses. The concentrations of the solutes were determined by an HPLC analysis The measured concentration of 37 mg/L compares remarkably well with the measured value of 40 mg/L reported by Ho et al. (1976), for a Synthane fluid-bed gasifier. The reported solubility of 2-naphthol in water is

TABLE II-9

COMPOUNDS IDENTIFIED IN THE METC RUN-101 CONDENSATE WATER

Compounds	Presence Confirmed By Method	Concentration Measured By Method
Hydroxybenzenes:		
Phenol	1,2,3	a
o-Cresol	2,3	a
m-Cresol	2,3	a
p-Cresol	2,3	a
2,3-Xylenol	2,3	a
2,4-Xylenol	2,3	a
2,5-Xylenol	2,3	a
2,6-Xylenol	2,3	a
3,4-Xylenol	2,3	a
3,5-Xylenol	2,3	a
Dihydroxybenzenes:		
Catechol	1	a
Resorcinol	1	a
Hydroquinone	1	a
4-Methyl Catechol	1	a
*Napthols:		
1-Naphthol	1,3	c
2-Naphthol	1,3	c
5,5-Dimethyl Hydantoin	1,3	a
*Low-Molecular-Weight Solutes:		
Acetic Acid	2,3	ND
Acetone	2	b
Acetone Cyanohydrin	2,3	ND
Acetonitrile	2	b
Methanol	2	b
*Thiocyanate	4	(Section II-A-2d)
*Polysulfide	(Section II-A-2e)	(Section II-A-2e)

Key:		
	(1) HPLC Co-chromatography	(a) HPLC
	(2) GC Co-chromatography	(b) GC (Packed)
	(3) GC-MS	(c) GC (Capillary)
	(4) MS-Probe	(ND) Not Determined

TABLE II-10

ANALYSIS OF METC RUN-101 CONDENSATE WATER

	Concentration (mg/L)	% COD	% TOC
Hydroxybenzenes:		85.7 %	93.7 %
Phenol	1,380		
Cresols	1,990		
Xylenols	840		
Dihydroxybenzenes:		2.4 %	2.8 %
Catechol	40		
4-Methyl Catechol	40		
Resorcinol	65		
Hydroquinone	4		
Naphthols	37	0.8 %	0.9 %
5,5-Dimethyl Hydantoin	20	0.2 %	0.3 %
Low-MW Organic Compounds:		1.5 %	1.6 %
Acetone	60		
Acetone Cyanohydrin	ND		
Acetonitrile	65		
Acetic Acid	ND		
Methanol	0		
*Thiocyanate	209 [370]	1.9 %	1.4 %
*Polysulfide Sulfur	[104]	3.0 %[1]	0.0 %
Identified COD/TOC (%)		95.8 %	100.7%
Measured COD/TOC (mg/L)		12,250	3,490
Organic Nitrogen (mg/L)[2]	120 (94 % Identified)		
Organic Sulfur (mg/L)[2]	404 (100 % Identified)[1]		

Values in brackets are for a nonacidified sample that had aged.
ND = Not Determined.

(1) Assuming polysulfides are in the form SS^{2-}.
(2) Nitrogen and Sulfur Balances are Based on Nonacidified Samples That Had Aged.

74 mg/L at 25 C (Perry and Green, 1984); therefore, the concentration of naphthols would not be expected to be much larger than the measured value in any case.

The low-molecular-weight compounds were identified using gas chromatography of the aqueous condensate sample. The presence of acetone, acetonitrile, and methanol was first confirmed by co-chromatography on a packed Porapak-Q column and later by co-chromatography on DB-17 and DB-Wax capillary columns. Acetone cyanohydrin and acetic acid were confirmed by co-chromatography and GC-MS analysis using a DB-Wax capillary column. On both the DB-17 and DB-Wax columns, the retention times for acetone, acetonitrile, and methanol were not much larger than that of water. Water eluted quickly on both columns and persisted in the mass spectometer cell, making it impossible to get an MS analysis of the acetone, methanol, and acetonitrile. The columns and the conditions for the identifications are described in Section II-A-2a.

Thiocyanate was identified as contributing to the measured COD, TOC, organic nitrogen, and organic sulfur analyses. The separation scheme used to identify thiocyanate in the condensate water was described in Section II-B-2g. Identification of thiocyanate was accomplished by employing high-resolution mass spectrometry to yield a molecular weight of 59 with an empirical formula of HSCN. The concentration of thiocyanate was determined via formation of a copper(II)-pyridine- thiocyanate complex as described in Section II-A-2d.

Table II-7b demonstrated that a concentration of 472 mg SCN^-/L (8.13 mmole SCN^-/L) was measured for the unacidified condensate water based on the uptake of organic nitrogen and organic sulfur onto an anion-exchange resin. Table II-10 reports that 209 mg SCN^-/L was measured in a preserved sample (pH 2) of condensate water and that 370 mg SCN^-/L was measured in an unacidified sample condensate water that had aged. The larger SCN^- concentration based on the anion exchange experiment was most likely due to the formation of SCN^- upon aging during storage and during the experiment.

The polysulfide analysis yielded a measured polysulfide sulfur concentration of 104 mg/L in the unacidified METC Run-101 sample. The polysulfide sulfur is only that sulfur existing in the zero oxidation state; however, the organic sulfur analysis includes both the sulfide and polysulfide sulfur. Therefore, some postulate must be made as to the extent of polymerization of the polysulfides in order to relate the polysulfide analysis to the measured organic sulfur. The results in Table II-10 assume a one-to-one stoichiometry between polysulfide sulfur and sulfide sulfur, that is, the polysulfides have been assumed to be present as disulfides (SS^{2-}) in the condensate water.

Including thiocyanate along with 5,5-dimethyl hydantoin and acetonitrile accounts for essentially 100% of the organic nitrogen measured in the condensate water sample. Thiocyanate and polysulfide (assumed to be SS^{2-}) together account for 100 % of the organic sulfur. Both thiocyanate and polysulfide also contribute to the measured COD of the sample. Polysulfide can react with cyanide to form thiocyanate and this is most likely the reason for the observed increase in thiocyanate for the condensate water sample upon aging. The mechanism of thiocyanate formation from polysulfides has been reported by Luthy et. al. (1979). The COD of polysulfides was calculated according to the following general reaction:

$$S_xS^{2-} + X\ H_2O + (3X+4)/2\ O_2 = SO_4^{2-} + X\ H_2SO_4 \quad \text{(Equation II-1)}$$

The above reaction was shown to be in good agreement with the measured COD's of sodium sulfide and sodium tetrasulfide solutions. It should be noted that the existence of thiocyanate and polysulfide can explain the lack of volatility (Table II-8) of the unidentified COD and its inability to be adsorbed (Table II-5 and Table II-6).

The compounds not denoted with an asterik in Tables II-9 and II-10 were compounds known to be present in the GFETC condensate water from previous analyses by Mohr and King (1983). All of these compounds were analyzed by HPLC, and their presence was confirmed by co-chromatography with standards in both the HPLC analysis and the capillary GC analyses, employing both the DB-Wax and the DB-17 capillary columns.

The experiments described in Section II-A-2e demonstrated that no significant amount of amino acids was present in the METC Run-101 condensate water. The presence of α-aminoisobutyric acid was suspected, since this compound can react with cyanate to form 5,5-dimethyl hydantoin, as described by Ware (1950). Ware also describes a mechanism where thiohydantoins can be formed from amino acids and thiocyanates. Amino acids are also zwitterionic (i.e., ionized at both high pH and low pH) and therefore are not detected by standard GC-MS techniques. Nevertheless, at least for the METC Run-101 sample, no amino acids were identified as being present.

The formation of hydantoins in condensate waters has received much attention in recent years. In 1981, Mohr and King were the first to discover the presence of 5,5-dimethyl hydantoin in a coal condensate water (Mohr and King, 1982, 1983 and 1985). Since then, Olson et. al. (1983) have confirmed the presence of 5,5-dimethyl hydantoin and other hydantoin derivatives in gasification condensate water. The kinetics of hydantoin formation have been studied by Deihl, Olson, and Worman (Deihl et. al., 1984; Olson et. al., 1985) and also by Grant (1985). Mohr & King postulated that 5,5-dimethyl hydantoin was formed in the condensate water from acetone, cyanide, and ammonium carbonate via the Bucherer-Bergs reaction (Bucherer and Fischbeck, 1934).

In the work presented here, the changes in concentrations of acetone and hydantoin upon aging were investigated. Analyses of two GFETC RA-106 condensate-water samples were compared, where one sample had been stored for 600 days at the pH of the collected sample (pH 9), and the other sample had been adjusted to pH 2 with sulfuric acid soon after sampling and then stored. The results demonstrated a difference of acetone concetration from 619 mg/L to 505 mg/L and 5,5-dimethyl hydantoin concentration from 230 mg/L to 460 mg/L between the pH 2 and pH 9 samples. These results indicate a 1:1 stoichiometric relationship between the amount of acetone decrease and the amount of 5,5-dimethyl hydantoin increase, for the pH 9 sample compared to the pH 2 sample. The findings are in agreement with the postulate of the formation of hydantoin via the Bucherer-Bergs reaction.

Both the joint efforts of Diehl, Olson, and Worman and those of Grant conclude that a model based on the Bucherer-Bergs reaction does fit the kinetic data well for hydantoin formation in the condensate water. Their results indicate that the reaction demonstrates pseudo second order kinetics, first order in both acetone and cyanide concentration, determined at a high constant concentration of ammonium carbonate.

II-C. CONCLUSIONS

The results presented in Table II-10 demonstrate complete identification of the compounds contributing to the TOC and 95.8% identification of those contributing to the COD. The identified COD is within the margin of error of the quantification of the various solutes and the accuracy of the COD measurements. Therefore, for practical purposes, the COD is essentially identified. Table II-10 shows that 100% of the organic-nitrogen containing compounds have also been accounted for in the analysis. In addition, essentially 100% of the organic sulfur measured for the sample can be accounted for if the polysulfide sulfur exists as disulfide ion (i.e., SS^{2-}).

Table II-11 presents the analysis of a condensate water received from the Great Plains Gasification Associates (GPGA) gasifier in Great Plains, North Dakota. Like the METC gasifier, the GPGA gasifier is a Lurgi low-temperature, fixed-bed gasifier. The analyses of the GPGA condensate water and the METC Run-101 condensate water differ in both the total organic content and the relative proportions of the compounds present in the samples. The GPGA sample had a much larger proportion of the low-molecular-weight organic compounds than the METC sample. Results earlier in this work demonstrated similarly high concentrations of the low-molecular-weight compounds for a Grand Forks Energy Technology Center (GFETC) condensate water (See Chapter I).

The analyses of GFETC condensate waters presented in Chapter I demonstrate that the composition of the condensate water varies with

TABLE II-11

ANALYSIS OF GPGA CONDENSATE WATER SAMPLED JUNE 14, 1985

	Concentration (mg/L)	COD (mg/L)	
Hydroxybenzenes:		18,520	(75.8 %)
Phenol	3,910		
Cresols	2,770		
Xylenols	760		
o-Methyl Phenols	70		
Dihydroxybenzenes:		1,170	(4.8 %)
Hydroquinone	50		
Catechol	450		
Resorcinol	40		
4-Methyl Catechol	70		
Naphthols	70		
Low-Molecular-Weight Organic Compounds:		3,030	(12.4 %)
Acetone	480		
Acetonitrile	110		
Acetic Acid	740		
Methanol	670		
Identified COD		22,900	(93.7 %)
Measured COD		24,430	(100. %)
Organic Nitrogen (mg/L)	37		
Organic Sulfur (mg/L)	150		

changes in the operating conditions of the gasifier and/or characteristics of the coal. Not enough information is available, for the samples we have received, to enable definite conclusions as to the relationship between the operating conditions, and/or coal properties, and the composition of the condensate water. However, based on the condensate samples that were analyzed in this work, plus those reported by Mohr and King (1985), it appears that gasification of the lower-grade coals leads to condensate waters with higher organic content due to the production of both more low-molecular-weight compounds and phenolics. Probstein and Hicks (1982) present the variation in elemental composition of coals with coal rank. Their results, presented as representative averages, demonstrate an increase in wt% oxygen content with decreasing rank of coal for lignite (24 wt%), subbituminous (21 wt%), bituminous (11 wt%), and anthracite (3 wt%). Weight-percents are on a moisture free basis. Both the GFETC and GPGA pilot plants were operated using a lignite coal and resulted in condensate waters with greater organic content than the METC condensate water,which was obtained from gasification of bituminous coal.

McClung and Geer (1979) present the total sulfur content of various coals, indicating the contribution of both pyritic sulfur and organic sulfur to the total sulfur analyses. The data demonstrate that in some cases the sulfur can vary much from place to place, even within a single seam. Furthermore, the data present no relationship between organic and pyritic sulfur, making it hard to draw any conclusions as to the effect of sulfur content on the condensate water composition without a detailed analysis of the particular coal used. However, based on the lack of organic sulfur compounds found in the condensate water, it appears that regardless of the form of the sulfur in the coal, the sulfur most likely leaves the gasifier as hydrogen sulfide, sulfur dioxide, hydrogen thiocyanate and elemental sulfur. As mentioned above in Section II-B-2, these compounds can lead to the formation of polysulfides and thiocyanate in the condensate water.

The variation of nitrogen in coal has not been as widely studied as the variation of sulfur. The amount of nitrogen present in the coal will have an impact on the amount of nitrogen-containing compounds formed in the condensate waters. The majority of the nitrogen in coal is converted in the gasification reactor to ammonia and hydrogen cyanide, much of which ends up in the condensate water. In this work, the amounts of nitrogen-containing organic compounds (i.e., acetonitrile, 5,5-dimethyl hydantoin, and acetone cyanohydrin) were found to be relatively small compared to the inorganic nitrogen compounds. Amines, particularly, and pyridines have been shown to be present in a number of oil-shale retort waters; however, amines are not generally found in gasification condensate waters to any great extent. The GC-MS determination of water-soluble primary amines is discussed by Avery and Junk (1985), where amines are identified as their pentafluorobenzaldehyde imine derivatives.. Applying this method to the METC Run- 101 condensate water resulted in detection of only a low level of aniline.

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CHAPTER III

ASSESSING TREATMENT ALTERNATIVES

III-A. Solvent Extraction

III-A-1. Theory of Solvent Extraction

III-A-1a. Extraction

The equilibrium distribution coefficient is a measure of the extent to which a solute will partition between two phases, at equilibrium. The equilibrium distribution coefficient is commonly expressed in either concentration units (K_c) , weight fraction units (K_d), or mole fractions units (K_x), as given by:

$$K_{ic} = c_{is}/c_{iw} \qquad \text{(Eq. III-1)}$$

$$K_{id} = w_{is}/w_{iw} \qquad \text{(Eq. III-2)}$$

$$K_{ix} = x_{is}/x_{iw} \qquad \text{(Eq. III-3)}$$

where c_i denotes concentration, w_i denotes weight fraction, and x_i denotes mole fraction for a component i, and the subscripts denote the solvent (s) and aqueous phases (w). K_{ic} and K_{id} are related to K_{ix} by:

$$K_{ix} = (M_s/M_w)\ K_{id} = (d_w/d_s)\ (M_s/M_w)\ K_{ic} \qquad \text{(Eq. III-4)}$$

where d is the density and M is the molecular weight of the respective phases.

The appropriate choice of units for the distribution coefficient depends on the particular application. The degree of chemical interactions can be more easily ascertained from examining the value of K_{ix}, in that K_{ix} is directly related to the activity coefficients of the solute in the solvent (γ_{is}) and the activity coefficient of the solute in the aqueous phase (γ_{iw}) by:

$$K_{ix} = x_{is}/x_{iw} = \gamma_{iw}/\gamma_{is} \qquad \text{(Eq. III-5)}$$

For extraction of organic solutes from water into organic solvents, the activity coefficient of the solute in the solvent phase is of the order of unity for many different solute-solvent pairs, and the aqueous-phase activity coefficient of the solute has a profound effect on the observed distribution coefficient. For solutes that have a low mutual solubility with water, the activity coefficient of the solute at infinite dilution (γ^{inf}) in the aqueous phase can be estimated from the mole-fraction solubility of the solute in water ($x_{iw}{}^{sat}$) by:

$$\gamma_i{}^{inf} = 1/x_{iw}{}^{sat} \qquad \text{(Eq. III-6)}$$

In general this relation holds true only for solutes that are soluble in water to less than 1 mole % and for those for which the solubility of water in the solute is similarly small. Equation III-6 becomes more accurate for solutes with lower mutual solubilities.

Concentration-based and weight-fraction-based distribution coefficients are more useful for comparison of solvents for process applications, in that the equipment costs associated with solvent extraction are related to the volume and the mass of solvent recirculated, and not necessarily to the number of moles of solvent.

solvents which exhibit solvent-solute interactions greater than simple van der Waals forces, the chemical functionality of the solvent plays an important role in determining the distribution coefficient. Typically for these solvents, as the organic chain length increases within a homologous series of solvents, the concentration and weight-fraction-based distribution coefficients also decrease, reflecting the decrease in density of functional groups per volume, or weight, of solvent. Concentration-based distribution coefficients are easier to determine experimentally, in particular for mixed-solvent or poorly characterized solvent systems, in that the average density or the average molecular weight of the solvent phase is not necessary for determination. The results presented in this work are reported in the three units defined above, depending on the particular system.

For the data presented here, the distribution coefficients were obtained from measurements of solute compositions in the aqueous feed and raffinate phases, along with the measured solvent-to-water ratio by:

$$K_d = (W/S)_{wt} * (w_f - w_r)/w_r \qquad \text{(Eq. III-7)}$$

where, wf and wr are the weight fractions of solute in the feed (f) and raffinate (r), and W and S are the relative weights of the aqueous phase (w) and the solvent phase (s). A similar relationship can be written for K_c, where the ratio W/S is expressed as a volume ratio. The second term in Equation III-7 is independent of the concentration basis. Equation III-7 holds for systems where the solvent and water do not exhibit appreciable mutual solubility. The values obtained from Equation III-7 are less precise at extreme S/W ratios, where a small mutual solubility can greatly change the S/W ratio during extraction.

The distribution coefficient is affected by changes in temperature and solute composition. For dilute solutions, generally less than 1 wt% solute in both aqueous and solvent phases, the distribution coefficient does not usually change with composition. The extraction of phenolics from water usually employs solvents with electron donating character so as to yield strong solute-solvent interactions. The solvents often contain hydrophobic alkyl groups to decrease their water solubility; therefore the molecular weights of these solvents are greater than that of water. The distribution coefficient for these solvents typically decreases at higher solute concentrations because reaching a loading limit in the solvent phase; however, in some cases the higher concentration of solute in the solvent phase can enhance extractability. The distribution coefficient at low concentrations is commonly referred to as the infinite-dilution distribution coefficient. The concentrations of the solutes investigated in this work are mostly below 1 wt%; therefore, the reported distribution coefficients can be considered as being close to those at infinite dilution.

III-A-1b. Back Extraction

Back extraction of solutes from solvents can yield information about the reversibility of the extraction and about the potential for regeneration via back extraction. If the solvent from a extraction is contacted with water at the same S/W ratio of the original extraction, a back extraction K_d (K_d^b) can be determined by:

$$K_d{}^b = (W/S)_{wt} * (w_f - w_r - w_r{}^b)/w_r{}^b \qquad \text{(Eq. III-8)}$$

where the variables are defined as above and $w_r{}^b$ is the weight-fraction of the solute in the back-extraction raffinate. Equation III-8 is subject to the same limitations as Equation III-7. For a reversible extraction at high dilution, K_d should equal $K_d{}^b$. Any irreversibilities in the extraction, such as chemical reactions, result in a larger value of $K_d{}^b$ than K_d. Lower values of $K_d{}^b$ than K_d indicate nonattainment of equilibrium during the extraction, material losses, or changes in conditions between the forward and backward extractions.

Solvent regeneration can be attained by altering the extraction conditions to provide a substantially lower distribution coefficient for the back extraction than for the forward extraction. In some cases this may be an ecomonmic alternative to distillative regeneration. Extraction of acidic solutes from water into organic solvents is generally pH dependent, in that typically only unionized species are extracted from the aqueous phase. For an aqueous pH > pK_a of the solute, the solute is principally ionized and prefers the aqueous phase. Therefore, successful back extraction of acidic solutes from solvent into water can be accomplished by raising the pH of the aqueous phase above the pK_a of the acid solute. A relationship between the distribution coefficient (K_d, low pH) obtained at a low pH (that is, a pH substantially lower than the pKa of the solute) and that obtained at a higher pH (K_d observed) is given by:

$$K_d \text{ (observed)} = K_d \text{ (low pH)}/\{1 + 10^{(pH-pK_a)}\} \qquad \text{(Eq III-9)}$$

where the pK_a is that of the solute being extracted. Equation III-9 demonstrates that the observed K_d decreases by approximately an order of magnitude for each unit of pH greater than the pK_a. This relationship will be used later in the discussion of regeneration of solvents using aqueous bases.

III-A-2. Extraction Experiments

Batch extraction experiments were performed by first preparing an aqueous feed solution of a solute at a known concentration, and then contacting the feed solution and solvent at a measured solvent-to-water ratio (S/W). After equilibration, the solute concentration in the feed and raffinate phases were determined, and the equilibrium distribution coefficient was calculated through the use of Equation III-7.

In this work, the phases were contacted in 15 mL amber glass vials fitted with teflon seals in the caps to prevent absorption into the cap lining. Both solvent and aqueous phases were measured into the vials via a 25 ml buret. Due to the small total volumes of the phases used in the experiments, the accuracy and reproducibility of the experiments were highly dependent on the precision to which the volumes of the phases were measured. Hence, the buret was found to yield more reproducible results than those obtained using a volumetric pipet. The phases were contacted in a shaking water bath to equilbrate for over 2 hours. After agitation, the vials were placed directly into a centrifuge and centrifuged for approximately 5 minutes. The aqueous phase was drawn off with a glass syringe and placed in a 25 mL scintillation vial with a foil-lined cap for later HPLC analysis. Equation III-7 allowed direct use of integration areas of the solute peaks obtained from chromatography, in place of the weight fraction, to yield the value of K_d. Description of the equipment used and the HPLC analysis are as previously described in Chapter II. The conditions for the extraction experiments are summarized in Appendix F. The effect of solvent extraction conditions on the measured equilibrium distribution coefficient is discussed in more detail by Senetar (1982).

III-A-3. Discussion of Extraction Results

III-A-3a. Hydroxybenzenes

Presented in Table III-1 are measured equilibrium distribution coefficients for extraction of condensate-water solutes into methyl isobutyl ketone (MIBK) at 30 C, along with literature values for the extraction of these solutes into diisopropyl ether (DIPE). The values in Table III-1 were measured for individual solutes in water rather than actual condensate waters. The distribution coefficients into MIBK are larger than those reported for extraction into DIPE. The relative merits of MIBK compared to DIPE have been discussed by Greminger et. al. (1982), where the authors also report a measured K_d of approximately 100 for phenol into MIBK at 30 C, and a K_d of 18.7 for catechol into MIBK at 25 C. Their values are in good agreement with those presented in Table III-1.

The data in Table III-1 demonstrate a trend of increasing K_d with increasing methyl substitution (i.e., going from phenol to cresol, to xylenol). The increase in K_d is most likely due to an increase in the aqueous-phase activity coefficient with the increase in hydrophobic methyl groups. Phenol is the least extracted of the hydroxybenzenes; however, phenol displays a large enough distribution coefficient to be

TABLE III-1

MEASURED WEIGHT FRACTION BASED DISTRIBUTION COEFFICIENTS (K_D) FOR EXTRACTION OF CONDENSATE-WATER SOLUTES INTO MIBK AND DIPE.

Solutes	DIPE(1)	MIBK(2)
Hydroxybenzenes:		
Phenol	36.5	84.9
m-Cresol		247.
p-Cresol		229.
2,3-Xylenol		611.
2,4-Xylenol		436.
2,6-Xylenol		576.
3,5-Xylenol		814.
Dihydroxybenzenes:		
Catechol	4.9	20.3
Resorcinol	2.0	18.0
Hydroquinone	1.0	9.9
5,5 Dimethyl Hydantoin		0.24

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(1) Data taken at 25 C, Greminger (1979).

(2) Data taken at 30 C.

easily extracted into either DIPE or MIBK.

III-A-3b. Dihydroxybenzenes

Dihydroxybenzenes are not extracted well into either DIPE or MIBK compared to the hydroxybenzenes, owing to the increased hydrophilic nature of the dihydroxybenzenes. Tsonopoulos (1970) reports infinite-dilution activity coefficients of 1.90, 0.61, and 4.3 for catechol, resorcinol, and hydroquinone, respectively, in water at 25 C. The results for both DIPE and MIBK extractions demonstrate rather suprisingly that, even though hydroquinone has the highest aqueous-phase activity coefficient of the dihydroxybenzenes, it is the least extracted. The extractability of catechol and resorcinol do follow the trend of higher values of K_d with greater aqueous-phase activity coefficient. The solvent-phase activity of the dihydroxybenzenes would not be expected to differ much between solutes; however, the lower K_d for hydroquinone suggests that it has a larger activity coefficient in the solvent phase than other dihydroxbenzenes. One possible explanation for the trend is that catechol and resorcinol may tend to dimerize in the solvent phase, while hydroquinone does so much less. Nevertheless, the trend for extraction of the dihydroxybenzenes into both DIPE and MIBK is consistent. Distribution coefficients for the dihydroxybenzenes into DIPE are low enough to require a large solvent-to-water ratio for removal of these compounds from the condensate water by DIPE extraction. MIBK would provide an equivalent removal of these compounds at a lower, but still substantial, solvent-to-water ratio.

Experiments were performed to identify alternative solvents that would yield larger distribution coefficients than MIBK for the extraction of dihydroxybenzenes from water. Listed in Table III-2 are the results of extraction experiments for the removal of hydroquinone and resorcinol from water into various solvents. Both lower-boiling and higher-boiling solvents were investigated. The dihydroxybenzenes have boiling points of 104 C, 110 C, and 173 C, respectively, for catechol, resorcinol, and hydroquinone. Lower-boiling solvents included furan (b.p. 32 C) and 4-methyl cyclohexanone (b.p. 170 C); while the higher-boiling solvents included benzophenone (b.p. 306 C), tributyrin (b.p. 305 C), and tributyl phosphate (TBP, b.p. 284 C), all in various diluents. Some of the less common solvents are illustrated in Figure III-1. All of the above solvents possess Lewis-basicity, the ability to donate electrons, through the oxygen atoms. The concepts of Lewis-acidity and Lewis-basicity of solvents have been discussed in detail by Jensen (1980). The physical properties of the solvents and diluents can be found in Appendix III-B.

Of the low-boiling solvents, 4-methyl cyclohexanone was found to have the highest distribution coefficient, over 2 times greater than that obtained with MIBK. Furan was investigated due to its very low boiling point and its suprisingly low water solubility (listed as being insoluble in water), contrasted to tetrahydrofuran (water miscible). However, furan was found to be a poor solvent for the extraction of hydroquinone (K_d <0.02). The low extraction K_d and the low water solubility of furan suggests that its molecules may preferentially interact with each other, rather than with hydroquinone or water.

TABLE III-2

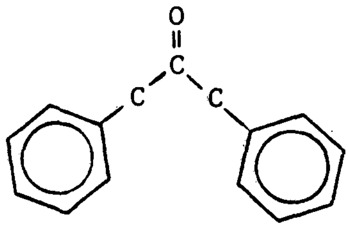
EXTRACTION OF HYDROQUINONE AND RESORCINOL INTO VARIOUS SOLVENTS AT 30 C

Solvent	Hydroquinone K_d	Resorcinol K_d
Low-Boiling Solvents		
4-Methyl Cyclohexanone	26.1	49.8
Methyl Isobutyl Ketone (MIBK)	9.9	20.3
Furan	<0.02	
High-Boiling Solvents		
Benzophenone (33 wt%) in Isobutyl Heptyl Ketone		2.3
Benzophenone (33 wt%) in Tributyrin		3.8
Tributyrin		4.3
Tributyl Phosphate (TBP)	166.	
TBP (50 wt%) in Dodecanol	30.2	
TBP (50 wt%) in Phenyl Ether	43.8	
TBP (50 wt%) in Hexadecane	58.0	

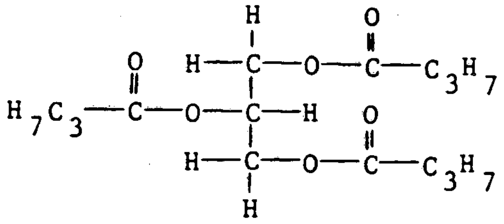
K_d = Weight-fraction based equilibrium distribution coefficient

FIGURE III-1

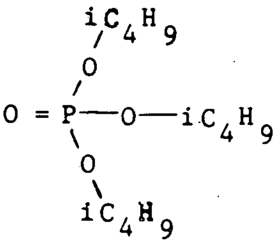
STRUCTURE OF SOME OF THE LESS COMMON LEWIS-BASE EXTRACTANTS INVESTIGATED



Benzophenone



Tributyrin



Tributyl Phosphate (TBP)

Neither benzophenone nor tributyrin yielded significant distribution coefficients for resorcinol. The relatively low K_d exhibited by benzophenone is most likely an effect of decreased basicity due to the aromatic ring in benzophenone, as compared to the aliphatic structure of MIBK for extracting hydroquinone (compare a K_x of 24.23 for the IBHK/benzophenone solvent versus a K_x of 53.3 for MIBK). Tributyrin was investiged due to its high degree of funtionality per mole of solvent (three ester groups per molecule); however, the lower basicity of the ester group, compared to a ketone group, yielded low values of K_d for tributyrin compared to MIBK. Steric hindrance may also play some part in the lower K_d for tributyrin.

Tributyl phosphate was the only high-boiling solvent which exhibited a favorable distribution coefficient for a dihydroxybenzene (K_d =166 for hydroquinone). The reversibility of the extraction was confirmed by back extraction of a TBP extract of hydroquinone back into water, which yielded the same high distribution coefficient. TBP was found to yield high distribution coefficients even when diluted to 50 wt% in various diluents. The most inert diluent, hexadecane, was found to yield the highest value of K_d, compared to other TBP-diluent mixtures. Use of dodecanol as a diluent yielded the lowest K_d for the diluents studied. The lower K_d for dodecanol can be attributed to hydrogen bonding between the -OH of the dodecanol and the =O of the TBP. This effect has also been observed by Bell (1980) for the extraction of phenol into tricresyl phosphate (TCP) using 2-ethyl hexanol as a diluent. Nevertheless, the K_d of 30.2 for the TBP-dodecanol mixture is still larger than the K_d yielded by MIBK. In addition, an extraction of phenol with 50 wt% TBP in dodecanol was found to yield a $K_d > 200$.

Burger (1984) presents the solubility of TBP in water for various TBP-diluent systems, as a function of TBP concentration. In general the more polar the diluent, the less TBP distributes into the aqueous phase. Judicious choice of a diluent for TBP would include a compromise between higher distribution coefficients for the solvent mixture and increasing TBP losses in the raffinate. An alcohol diluent may provide a favorable balance between distribution coefficient and solvent losses.

III-A-3c. Hydantoins

Table III-1 demonstrates that MIBK does not yield an appreciably large K_d for the extraction of 5,5-dimethyl hydantoin (5,5-DMH). The extractability of 5,5-DMH into various solvents has been studied by Mohr and King (1985), data from whom are presented in Table III-3a. The results demonstrate that extraction of 5,5-DMH into Lewis acid solvents (i.e., methylene chloride and di(2-ethylhexyl)phosphoric acid, D2EPHA) yielded values of K_d below 0.05. The Lewis-base solvents, with the exception of Adogen 363 (a tertiary amine, Sherex Chemical Co.), demonstrated higher distribution coefficients for 5,5-DMH. Also presented in Table II-3a are the values of K_x for the extraction of 5,5-DMH. In order of Lewis basicity Adogen 363 > TOPO > TBP > TCP > MIBK and for the observed K_x, TBP > TCP > TOPO > MIBK. TBP, TCP and MIBK demonstrate a trend of higher K_x with increasing basicity of the solvent. TOPO did not obey this trend. The data for TOPO are for a solvent mixture thereby making it difficult to draw any definite conclusions. K_x was not calculated for the Adogen 363-kerosene mixture; however, the very low K_d exhibited by this solvent mixture demonstrates

TABLE III-3a

EQUILIBRIUM DISTRIBUTION COEFFICIENTS (K_d and K_x) FOR EXTRACTION OF 5,5-DIMETHYL HYDANTOIN FROM WATER INTO VARIOUS SOLVENTS AT ROOM TEMPERATURE (MOHR AND KING, 1985)

Solvent	K_d	K_x
Lewis Acids:		
Methylene Chloride	<0.05	<0.14
25 wt% Di (2-ethylhexyl) Phosphoric Acid in Kerosene	<0.05	----
Lewis Bases:		
25 wt% Adogen 363 in Kerosene	<0.05	----
25 wt% Tri-n-Octyl Phosphine Oxide (TOPO) in Methyl Isobutyl Ketone (MIBK)	<1.2	2.50
Methyl Isobutyl Ketone (MIBK)	0.25	1.39
Tricresyl Phosphate (TCP)	0.11	2.24
Tributyl Phosphate (TBP)	2.6	38.4

TABLE III-3b

EXTRACTION OF 5,5-DIMETHYL HYDANTOIN FROM WATER INTO VARIOUS SOLVENTS

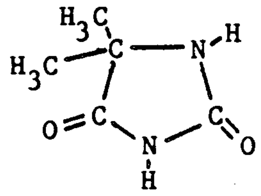
Solvent	K_d	K_x
Cyclohexanone	0.92	5.21
4-Methyl Cyclohexanone	0.61	3.80
2-Methyl Cyclohexanone	0.36	2.32
Methyl Isobutyl Ketone (MIBK)	0.24	1.33

K_d = Weight-fraction based equilibrium distribution coefficient.

K_x = Mole-fraction based equilibrium distribution coefficient.

that ionizing basicity is not useful for the extraction of 5,5-DMH.

The higher K_d's for the extraction of 5,5-DMH into Lewis bases rather than into Lewis acids demonstrated that 5,5-DMH had more Lewis-acid character than Lewis-base character. Furthermore, the low values of K_d obtained in the extractions suggested that 5,5-DMH could be a strong enough acid as to be partially ionized during the extraction experiments. The structure of 5,5-DMH is:



The hydrogen in the 3-position would be expected to be the more acidic, in that loss of the H^+ from the 3-position could be charge stabilized by resonance with both the adjancent carbonyl groups. Loss of a H+ in the 1-position could be stabilized through resonance with only one carbonyl group.

The pK_a of 5,5-DMH was measured in order to determine whether 5,5-DMH was dissociated during extraction. Two different techniques were employed to estimate the pK_a. The first technique involved the measurement of the extraction K_d at different pH values of the aqueous-phase. Extractions of 5,5-DMH into MIBK were carried out at pH 2, pH 7.01, pH 8.82, and pH 9.16, yielded K_d's of 0.22, 0.237, 0.166, and 0.099, respectively. The pK_a was calculated at the two higher pH values by assuming (1) that only the unionized solute would partition between the phases, and (2) that essentially no ionization of 5,5-DMH occured at the lowest pH (pH 2). The results yielded an estimated pK_a of 5,5-DMH between 9.01 and 9.19. Another estimate of the pK_a of 5,5-dimethyl hydantoin was obtained by dissolving 1000 mg 5,5-DMH in 1 L Milli-Q grade water, and calculating the pK_a based on the measurement of the aqueous pH. This method yielded a pK_a of 8.9. The pK_a of 5,5-DMH determined through these measurements was later verified by comparison with a value of 9.19 reported by Bateman (1980).

The relatively low pK_a of 5,5-DMH could help to explain the extraction results in Table III-3a. The extractions of Mohr and King were performed on dilute solutions of 5,5-DMH in Milli-Q grade water and were susceptible to changes in the aqueous-phase pH brought about by contacting the aqueous feed with the organic solvents. Adogen 363 is a Bronsted base, and when contacted with water it should raise the pH of the water above pH 7. Also, it is likely that water-soluble impurities may be present in Adogen 363 that raise the pH of the aqueous phase upon contacting the phases. TOPO is not strongly enough ionizing to raise the pH of the water appreciably; however, TOPO has been known to contain water-soluble impurities which can be basic in nature, depending on the grade of TOPO and the supplier.

The much higher value of K_d for TBP than TCP cannot be attributed to changes in the aqueous-phase pH. An extraction of 5,5-DMH from water into TBP (S/W ratio = 1.0) confirmed the relatively high K_d for TBP reported by King and Mohr. TCP has a decreased basicity compared to TBP due to the presence of the electron withdrawing aryl groups. However, the lower basicity of TCP cannot alone account for the difference between the K_d's exhibited by these solvents. The higher K_d for TBP may be related to the relatively high solubility of water in TBP (3.58 mol/L, Burger, 1984), essentially a 1/1 molar ratio of water to TBP. On the other hand, TCP has been reported to be insoluble in water (Perry and Green, 1984).

Table III-3b presents the effect of ketone structure on the measured extraction of 5,5-DMH from water, presented as K_x. The results indicate that the ketone with the least steric hindrance around the carbonyl, cyclohexanone, yielded the highest value of K_x. Methyl substitution at the ortho-position, relative to the carbonyl, was found to decrease the measured K_x to a greater extent than methyl substitution at the para-position. MIBK was found to have the smallest K_x of the ketones investigated, and also would be expected to be the most sterically hindered. The effect of steric hindrance on extraction equilibria has been investigated in more detail by Munson and King (1984).

As discussed in Chapter II, ketones can react with cyanide and ammonium carbonate to produce hydantoins, via the Bucherer-Burgs synthesis reaction. Since MIBK is a potential solvent for treating condensate water, the possibility of forming a hydantoin derviative of MIBK during the extraction of condensate water was investigated.

Grant (1985) reports that acetone cyanohydrin may be an intermediate to the formation of 5,5-DMH from acetone. Listed in Table III-4 are the equilibrium constants for the formation of cyanohydrins from cyanide for various ketones, obtained from data presented by Lurie (1980). Data were not reported for the formation of cyanohydrin from MIBK; however, one would expect it to display an equilibrium constant somewhere in the range of that of methyl t-butyl ketone and methyl isopropyl ketone.

An experiment was performed to test for the extent of formation of

TABLE III-4

EQUILIBRIUM CONSTANTS (K_{eq}) FOR THE FORMATION OF CYANOHYDRINS FROM CYANIDE AND VARIOUS KETONES AT 20 C

Ketone	K_{eq} (L/mole)
Acetophenone	0.775
Acetone	32.7
Methyl t-Butyl Ketone	32.1
Methyl Ethyl Ketone	37.9
Methyl Isopropyl Ketone	65.4
Cyclohexanone	1087.

5-methyl, 5-isobutyl hydantoin from MIBK, cyanide, and ammonium carbonate. A mixture containing 0.25M ammonium bicarbonate and 1000 mg/L cyanide (added as potassium cyanide) was saturated with MIBK and placed in a constant temperature bath at 30 C. The solution was removed from the bath after 24 hours had elapsed, and then analyzed by HPLC for the presence of the hydantoin derivative. No measureable amount of hydantoin was found to be formed. The retention time for the hydantoin derivative was obtained for comparison by preparing the hydantoin derivative of methyl isobutyl ketone via the Bucherer-Burgs synthesis as decribed by Ware (1950). In addition, the rate of formation of the hydantoin derivative of MIBK was estimated using the reaction rate parameters obtained by Grant (1985) for the formation of 5,5-DHM from acetone. The calculation confirmed that only a very small amount of the derivative (i.e., approximately 28 mg/L) should have formed in the 24 hour period at 30 C. Therefore, it appears that the formation of hydantoins from MIBK during extraction should not be a limitation to the use of MIBK for treatment of the condensate waters.

III-A-3d. Regeneration By Back Extraction

Back extraction of extracted solutes from solvent into aqueous bases (both sodium hydroxide and ammonia) was examined as a regeneration alternative for TBP. In particular, the use of ammonia for solvent regeneration is of interest since ammonia is a recovered byproduct from the condensate water treatment. Listed in Table III-5 are the pK_a values of various condensate water solutes. Note that all of the compounds listed in Table III-5 display values of pK_a between 9.19 to 10.35.

TABLE III-5

pK_a VALUES* OF VARIOUS CONDENSATE-WATER SOLUTES

Solute	Temperature	pK_a
5,5 Dimethyl Hydantoin#	25 C	9.19
Resorcinol	25 C	9.81
Catechol	20 C	9.85
Phenol	20 C	9.89
m-Cresol	25 C	10.01
p-Cresol	25 C	10.17
o-Cresol	25 C	10.20

---

* Values from Weast (1984) unless otherwise indicated.

Bateman (1978).

As discussed earlier, Equation III-9 demonstrates that substantial reduction in the distribution coefficient for the forward extraction can be attained by back extraction of acidic solutes into an aqueous base which has a pH significantly greater than the pK_a of the solutes. Experiments were performed using a solvent mixture of 50 wt% TBP in dodecanol to extract phenol from water, followed by back extraction into either 1M NaOH or various concentrations of aqueous ammonia. The original phenol concentration in the feed was 1000 mg/L, and the same solvent-to-water ratio was used in both the forward and the back extractions. HPLC analysis was performed on the aqueous feed and the raffinates from both the forward and back extractions. Originally an analysis of the extract was also performed by diluting the organic phase in methanol and performing an HPLC analysis; however, the extract analysis was found to be unreliable for solutions which had contacted aqueous ammonia, since the UV absorbance (at 280 nm) of the phenol peak for the extract analysis increased after contacting the extract with aqueous ammonia. This increased absorbance may have been due to the formation of phenol decomposition products. Nevertheless, the results based solely on aqueous analyses were reproducible, and for the case of using NaOH as a regenerant, an extract analysis confirmed a material balance closure.

Phenol was found to be essentially 100% back extracted into 1M NaOH. Back extraction of phenol into aqueous ammonia was found to be significantly less, and dependent on the aqueous-phase ammonia concentration. The results for the ammonia regeneration for the TBP-dodecanol-phenol system are presented in Table III-6 as the percent solvent regeneration attained for a batch back extraction at the

TABLE III-6

REGENERATION OF SOLVENT-PHENOL EXTRACTS WITH AQUEOUS AMMONIA AT 30 C

Concentration of Ammonia	Percent Regeneration	pH	Back Extraction K_c Measured	Back Extraction K_c Predicted
50 wt% Tributyl Phosphate/ 50 wt% Dodecanol*				
0.5 N	0.0 %	11.5	>100.	5.0
2.0 N	8.2 %	11.8	5.0	2.5
8.0 N	18.7 %	12.1	1.7	1.9
14.2 N	21.6 %	12.2	1.3	1.0
Methyl Isobutyl Ketone (MIBK)#				
1.0 N	29 %	11.6	1.62	1.53

K_c = Concentration based equilibrium distribution coefficient.

* K_c measured at a solvent-to-water ratio of 2.0.

K_c measured at a solvent-to-water ratio of 1.0.

indicated pH. At the pH of 11.5, phenol is almost 98% ionized; however, only a fraction of the phenol goes into the aqueous phase at this and slightly higher values of pH. Also entered in Table III-6 are the measured equilibrium distribution coefficient for the back extraction, expressed as K_c, and the back extraction K_c predicted by Equation III-9. The equilibrium distribution coefficient at low pH for phenol into the TBP-dodecanol solvent mixture was experimentally determined as ~210. There is general agreement between the experimentally determined value of K_c and that predicted by Equation III-9 using a K_c at the low pH of 210. The results indicate that even at $(pH - pK_a) = 2$ (i.e, factor of 100 decrease in K_d), the distribution of phenol still favors the organic phase.

Also listed in Table III-6 are the results for the back extraction of phenol into MIBK, demonstrating that back extraction for MIBK was also much less than complete, but nevertheless in agreement with that predicted using Equation III-9. Similar results were also demonstrated using isobutyl heptyl ketone (IBHK) and 2,6-dimethyl cyclohexanone as solvents. As with the TBP-dodecanol mixture, MIBK also yielded 100% regeneration when contacted with 1M NaOH. The ketone solvents also display very large distribution coefficients for extracting phenol at low pH.

In order to benefit from the use of ammonia for regeneration, the solvent must have a high enough distribution coefficient to extract the solutes in the primary extractor at a low S/W ratio, but must still exhibit a low enough distribution coefficient at the pH of the ammonia solution to allow back extraction at a reasonably low S/W ratio. Regeneration with ammonia solutions yields a difference of 2 logarithmic units between the pH of the regenerant solution and the pK_a of the solutes. Working with a difference between the pH and pK_a of about 2, the desirable K_d for the forward extraction may be in the range of about 10 to 20 to yield a back-extraction K_d of about 0.1 to 0.2. Since extraction of the condensate water solutes displays a wide variation in K_d from solute to solute, back extraction into base may be appropriate for only a particular class of compounds, such as dihydroxybenzenes. An optimal K_d can be attained by changes in the extractant concentration and the type of diluent.

III-B. Adsorption

III-B-1. Theory

Adsorption generally involves the transfer of one or more solutes from a fluid phase to an interface. For adsorption of solutes from water onto solid adsorbents, solutes accumulate at the solid-liquid interface, thereby providing a separation. Since the amount of adsorption depends on the surface area available, adsorbents with the highest surface area per unit volume may be preferred. Typical activated carbons are highly porous and have surface areas near 1000 m^2/g. Adsorption has been widely investigated both theoretically and experimentally. Adsorption theory has been summarized by Parfitt and Rochester (1983), Kipling (1965), and Adamson (1982), among others. In addition, Vermeulen et. al. (1984) present an overview of adsorption theory and technology.

Adsorption is similar to extraction, in that solutes with higher activity coefficients in water are usually more preferentially removed from solution. However, unlike extraction, a new phase is formed during adsorption (i.e., an adsorbed layer), and the free energy of this phase is related to its surface tension rather than to its activity coefficient. The motive force for adsorption is a decrease in total surface free energy. Surface tension is simply a measure of the partial molar Gibbs free energy.

Adsorbents, like extractants, vary in chemical funtionality and exhibit different degrees of affinity for various solutes. The adsorption of organic molecules from aqueous solution often takes advantage of van der Waals interactions between the solute and the adsorbent. Specific solute-adsorbent interactions may develop through such mechanisms as hydrogen bonding, electostatic interactions, or even chemical reaction.

In this work, both an activated carbon and a synthetic resin were investigated for the removal of catechol and 5,5-dimethyl hydantoin from aqueous solution. Both of these solutes are polar in nature and very difficult to remove from water due to their low aqueous-phase activity coefficients.

III-B-2. Adsorption Experiments

Batch adsorption experiments were performed to assess capacity and regenerability of both Witcarb 950 (activated carbon, 12x30 mesh, Witco Chemical) and Amberlite XAD-7 (acrylic ester polymer, Rohm & Haas) for the adsorption of catechol and 5,5-dimethyl hydantoin (5,5-DMH). A weighed amount of adsorbent (about 1 g) was placed into a 20 mL scintillation vial and contacted with 10 mL of Milli-Q grade water containing either dissolved catechol or 5,5-DMH. The vial was placed in a shaking water bath at 30 C overnight to equilibrate. After equilibration, the resin was poured from the vial into a fritted glass funnel (medium porosity) set inside a 50 mL plastic centrifuge tube, and then centrifuged for 5 to 10 minutes to remove the supernatant liquid. The glass funnel was covered with Parafilm (American Can Co.) during centrifugation to prevent evaporative loss of water. HPLC analyses of the original feed solution and the resulting supernatant liquid were performed to determine the extent of adsorption at the measured equilibrium liquid composition. The HPLC analyses were performed as previously described in Chapter II.

As shipped, commercial adsorbents often contain impurities. The adsorbents used here were washed thoroughly to remove impurities before use. The adsorbents were first washed with methanol (500 mL/ 100 g adsorbent) and then rinsed extensively with Milli-Q grade water (4 L/ 100 g adsorbent). The adsorbents were then dried in a vacuum drying oven (77 C and near 200 mm Hg absolute) for three days. The adsorbents were prewet with water and centrifuged as described above before use. Prewetting the adsorbents was found to maintain a constant liquid volume during adsorption, thereby making it simple to measure the amount of solute adsorbed and that remaining in solution. The dry weight of adsorbent used was obtained by drying the adsorbent in the vacuum drying oven after use and weighing the dried adsorbent. The adsorption measured in this way was found to be in agreement with that determined using the composite isotherm equation for a binary liquid system (see for example Adamson, 1982).

Desorption experiments were performed to evaluate the use of solvent regeneration of the adsorbents. For desorption experiments, the adsorbents previously used for the adsorption experiments were contacted with 10 mL of regenerant solution, as described above. The resulting regenerant solution was analyzed through the use of HPLC. Methanol, acetone, and aqueous ammonia were investigated for regeneration of Witcarb 950. Methanol only was used to regenerate the XAD-7 resin.

III-B-3. Discussion of Adsorption Results

III-B-3a. Witcarb 950

The results of the adsorption experiments described above indicated that both catechol and 5,5-dimethyl hydantoin were adsorbed to a high degree by Witcarb 950. After equilibration of Witcarb 950 with the feed solution, no measurable amount of either solute was found in the supernatant liquid (removal > 99.9%).

Regeneration of Witcarb 950 by solvent regeneration with acetone, methanol, and aqueous ammonia was found to be ineffective. However, although 5,5-DMH was also adsorbed to a high degree, regeneration by desorption in methanol was found to recover essentially 100% of the adsorbed 5,5-DMH. The irreversible adsorption of catechol onto Witcarb 950 is in agreement with the well known difficulty encountered in regeneration of activated carbon after phenol adsorption (Chapter I).

The ability of methanol to regenerate Witcarb 950 indicates that 5,5-DMH does not form any strong chemical interactions with the surface of the activated carbon. Solvent regeneration would be useful only if the hydantoin could be first isolated from phenolics before adsorption. This may be difficult to accomplish since the phenolics are the most abundant species in the condensate water, and trace amounts are likely to be present in any case.

III-B-3b. Amberlite XAD-7

The adsorption results for catechol and 5,5-DMH are summarized in Figure III-2. Although the data do not cover a vary wide range of concentrations, they demonstrate that catechol is adsorbed to a greater extent than 5,5-DMH. The lower adsorption of 5,5-DMH than catechol may be due to a lower aqueous-phase activity coefficient for 5,5-DHM, as evidenced by the low extraction distribution coefficients also obtained for 5,5-DMH. The Amberlite XAD-7 resin displayed a much lesser adsorption for both of the solutes than did Witcarb 950. The solute concentrations in equilibrium with Amberlite XAD-7 could be quantified; however, the concentrations in equilibrium with the Witcarb 950 were too small to be measured.

Both catechol and 5,5-DMH were found to be completely desorbed from the Amberlite XAD-7 into methanol. The ability to permit solvent regeneration of both catechol and 5,5-DMH favors the use of the polymeric resin rather than an activated carbon. The lower adsorption of these solutes onto Amberlite XAD-7 would however require a larger volume of adsorbent and/or more frequent regenerations than if activated carbon were used, leading to increased treatment costs.

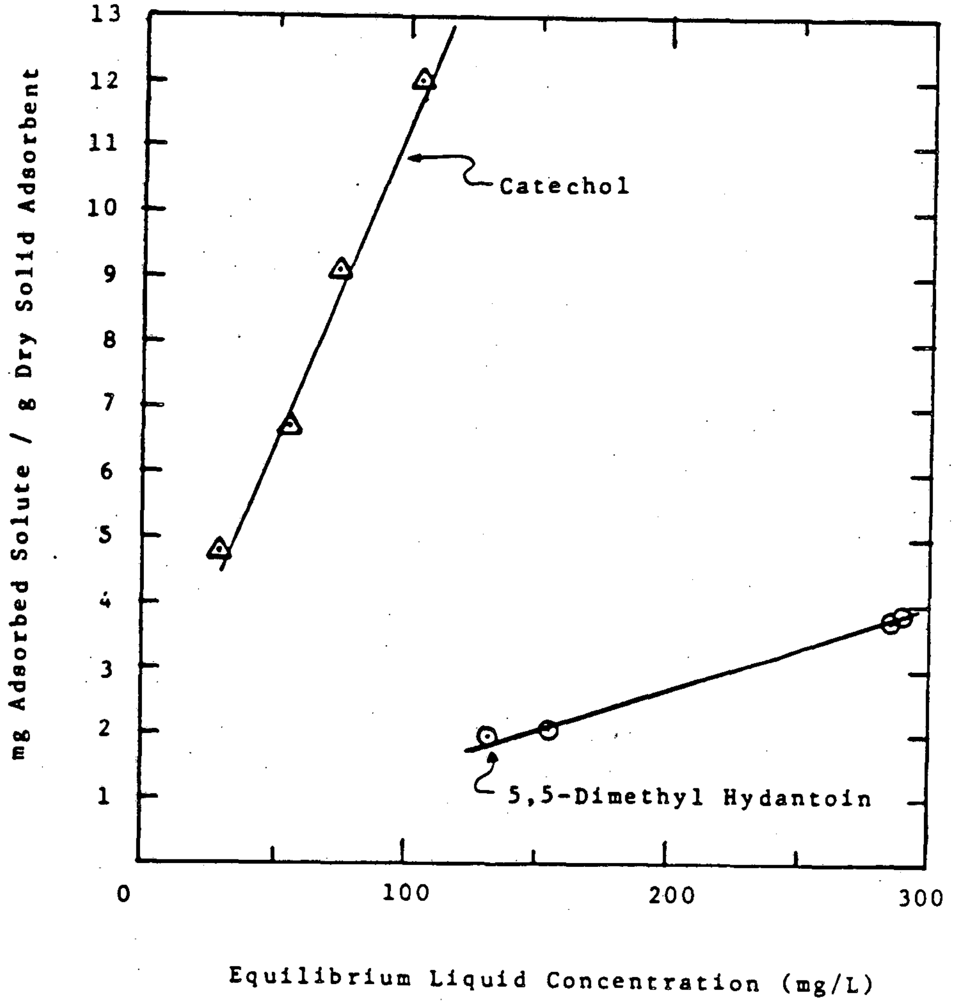
III-C. Anion-Exchange

III-C-1. Theory

The theory of ion-exchange has been discussed by Helfferich (1962) and Vermuelen et. al. (1984). Ion exchange involves transfer of ions from one phase to another in exchange for the transfer of a charge equivalence of ions in the opposite direction (i.e., both phases remain balanced in charge). Anion exchange involves the transfer of anions

FIGURE III-2

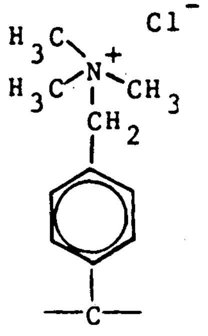
ADSORPTION OF CATECHOL AND 5,5-DIMETHYL HYDANTOIN ON AMBERLITE XAD-7



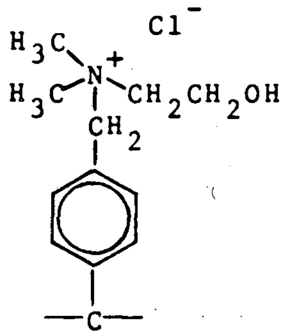
between phases, and cation exchange involves the transfer of cations. An ion exchanger can be a either a solid or a liquid that is capable of exchanging ions. Ion exchangers typically exhibit different degrees of affinity for various ions, and therefore can be selective. Discussed below is the applicability of anion exchange for the removal of thiocyanate from water. Much of the discussion will be presented for solid anion exhangers (i.e., polymeric resins); however, most of the concepts can be applied to liquid anion exchangers as well.

III-C-1a. Strong-Base Anion Exchange Resins

The use of anion exchange relies on the ionic nature of the anion exchange resin. Strong-base anion exchange resins possess their ionic character regardless of the pH of the medium. These resins typically have quaternary ammonium groups with ionically bonded anions, and are furnished commercially in either OH^- or Cl^- forms. The strong base resins are commonly manufactured in two different types as illustrated below:



TYPE I



TYPE II

Examples of type I resins are AG1 (Bio-Rad Laboratories), Dowex 1 or SBR (Dow Chemical), while common type II resins are AG2 (Bio-Rad Laboratories), Dowex 2 or SAR (Dow Chemical). Type I and type II resins demonstrate different degrees of selectivity among anions. Table III- 7 presents the relative selectivities of various anions to hydroxide ion for AG1-X8 and AG2-X8 resins, as reported by Bio-Rad Laboratories (1985). The relative selectivities reported in Table III-7 are measured as the bed volumes of 1 M NaOH required to regenerate a bed that had been fully loaded with the particular anion. Therefore, these relative selectivities are of use more from a practical standpoint rather than a theoretical one, since the relative affinities of the ions for the anion-exchange resin can be affected by the aqueous phase and resin compositions. Changes in selectivity of anion exchange resins with concentration have been described by Helfferich (1962).

Both type I and type II resins are frequently manufactured as styrene-divinyl benzene copolymers with various physical structures (e.g., porous gel or macroporous bead). The effect of resin structure on the regenerability and fouling characteristics of anion-exchange resins has been discussed by Dow Chemical (1983).

III-C-1b. Weak-Base Anion-Exchange Resins

Weak-base resins typically have tertiary amine funtionality, and therefore are limited in application to media with pH significantly less than the pK_a of the amine group on the resin. At low pH the weak-base resin will accept a proton, and along with it a counterion, an anion, from the aqueous phase in order to maintain electroneutrality, as indicated by:

$$[A] + (HY) \longrightarrow [AHY] \qquad \text{(Eq. III-10)}$$

TABLE III-7

RELATIVE SELECTIVITIES OF AG1-X8 AND AG2-X8 ANION EXCHANGE RESINS (BIO-RAD LABORATORIES,1983)

Anion	Relative Selectivity AG1-X8	AG2-X8
I^-	175.	17.
Phenolate	110.	27.
HSO_4^-	85.	15.
ClO_3^-	74.	12.
NO_3^-	65.	8.
Br^-	50.	6.
CN^-	28.	3.
HSO_3^-	27.	3.
BrO_3^-	27.	3.
NO_2^-	24.	3.
Cl^-	22.	2.3
HCO_3^-	6.0	1.2
IO_3^-	5.5	0.5
HPO_4^-	5.0	0.5
Formate	4.6	0.5
Acetate	3.2	0.5
Propionate	2.6	0.3
F^-	1.6	0.3
OH^-	1.0	1.0

---

* Selectivities Relative to OH^-

where A is the amine, and Y is any anion present. The brackets, [], indicate the organic or resin phase, and the parentheses, (), indicate the aqueous phase. An equilibrium constant for the reverse of the above reaction can be expressed as:

$$K_a = [A]\ (H^+)\ (Y^-)/\ [AHY]. \qquad \text{(Eq. III-11)}$$

Once the resin is converted into the ion-pair form, the resin can be used as an anion exchanger. The anion exchange process can be written as:

$$[AHX] + (Z^-) \longrightarrow [AHZ\} + X^- \qquad \text{(Eq. III-12)}$$

where X^- and Z^- are anions competing for the available exchange sites. A mass-action expression:

$$K_{zx} = [AHZ]\ (X^-)\ /\ [AHX]\ (Z^-) \qquad \text{(Eq. III-13)}$$

can be written for the anion exchange process, where K_{zx} is referred to as the selectivity coefficient. Helffrich (1962) demonstrates that the selectivity coefficient can vary in some cases for a strong-base anion exchanger as a function of ionic composition of the resin. For sake of argument, the value of K_{zx} will be considered to be constant to enable further development. Also, it should be noted that the equations developed here are not directly applicable when multi-valent ions and ions of different valencies are present.

For a binary system, Equation III-13 can be related to Equation

III-11 by setting the total anion concentrations in each phase equal to the sum of the individual anions, as:

$$(Y^-) = (X^-) + (Z^-) \qquad \text{(Eq. III-14)}$$

and

$$[AHY] = [AHX] + [AHZ]. \qquad \text{(Eq. III-15)}$$

Furthermore, the total amine groups present on the resin, $[A_t]$, can be set equal to the sum of the unoccupied groups plus those occupied by either anion, as given by:

$$[A_t] = [A] + [AHX] + [AHZ] \qquad \text{(Eq. III-16)}$$

The above expressions can be combined to yield the fraction of amine sites that are occupied by the component Z^- through the following relationship:

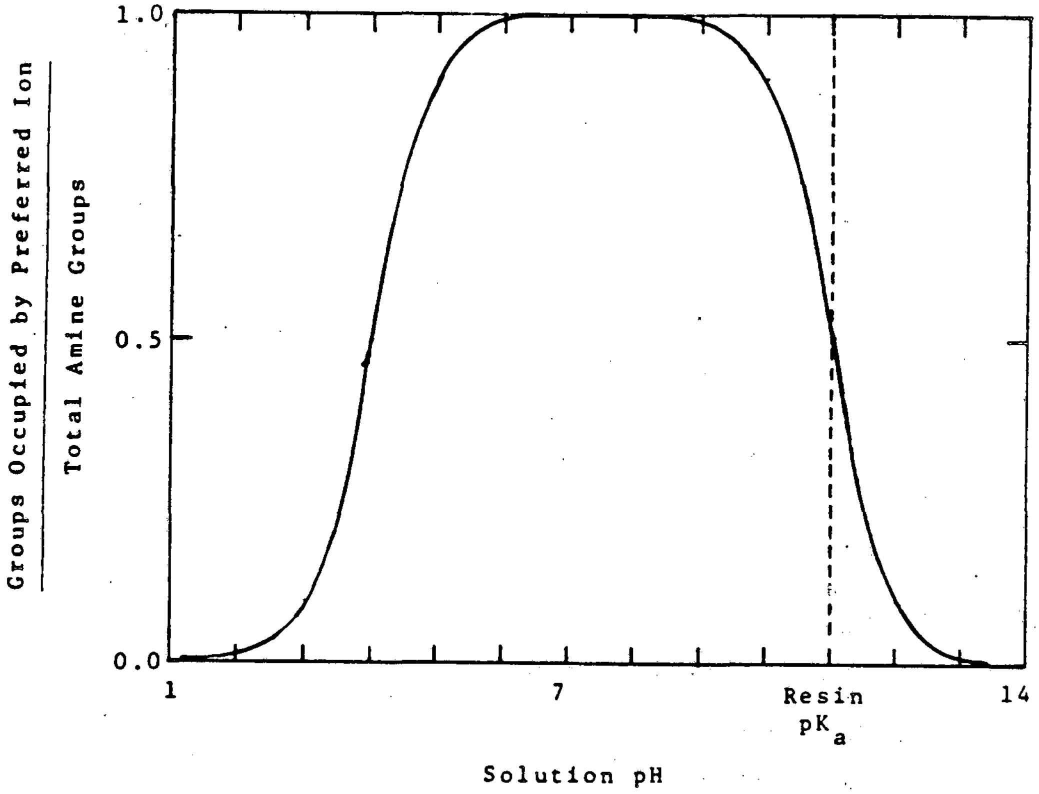
$$R = \frac{[AHZ]}{[A_t]} = \frac{(H^+)\,K_{zx}}{\{(K_a/[(X^-)+(Z^-)]\}\ \{K_{zx} + [(X^-)/(Z^-)]\}} \qquad \text{(Eq. III-17)}$$

Figure III-3 illustrates the general shape of the above relationship as a function of pH.

At very low pH, $(H^+) >> K_a$ and $(X^-)/(Z^-) >> K_{zx}$, resulting in the expression:

FIGURE III-3

CHANGE IN ANION LOADING VERSUS pH OF MEDIUM FOR A WEAK-BASE RESIN



$$R = K_{zx}\,(Z^-)/(X^-) \qquad \text{(Eq. III-18)}$$

where, X^- is considered to be the acid counterion. Therefore, the decrease in R with decreasing pH is due to the increased competition of acid counterions for the available ion-exchange sites. Such an effect would not be observed if an experiment were carried out at constant ionic strength of the acid counterion (i.e., by the addition of a salt of the acid).

As the pH is increased to the middle pH range, less acid counterions are present, and the ratio $(X^-)/(Z^-)$ becomes very small, resulting in $R = 1$. This is as would be expected since there would be essentially no competition for the available anion-exchange sites. Again, if the experiment is performed at a constant composition of X^-, the value of R would be less than 1, and its value would depend on the value of K_{zx} and the ratio of ion concentrations.

Finally, the decrease in R at high pH is due to the loss of anion-exchange sites, caused by the dissociation of the conjugate acid of the amine, and can be expressed as:

$$R = (H^+)\ /\ \{[K_a/[(X^-)+(Z^-)]] + (H^+)\} \qquad \text{(Eq. III-19)}$$

when $K_{zx} \gg (X^-)/(Z^-)$. Equation III-19 demonstrates that weak-base anion exchange resins could only be applicable at values of pH substantially less than the pK_a of the amine.

III-C-2. Ion-Exchange Experiments

Fixed-bed studies were performed to assess the capacity and regenerability of resins for thiocyanate removal. The experiments employed 2 mL of resin packed in a 10 mL Econo-Column (Bio-Rad Laboratories). The adsorption capacity of the resins was obtained by passing 10 mL of 1200 mg SCN^-/L (as KSCN) through the column and measuring the thiocyanate in the effluent. Likewise, the regeneration was measured by passing 100 mL of the regenerant solution through the column and measuring the thiocyanate that was eluted. Thiocyanate is reported to form neutral solutions when dissolved in water (Windholz, 1983); therefore, the original feed solution can be assumed to have a pH near 7. Both the feed and regenerant solutions were passed slowly through the bed (approximately 2 mL/min) in order to attain near equilibrium between the interstitial liquid and the bed. Thiocyanate determination was performed as described in Chapter III. Before use, the resins were thoroughly washed with Milli-Q grade water.

In some cases the resins were converted to a particular ionic form before use (e.g., OH^- form) by washing the resins with 100 mL of solution containing the particular anion at a high concentration. Conversions to the OH^-, HCO_3^-, Cl^- forms were accomplished using 1 N NaOH, 1 N NH_4HCO_3, and 1 N HCl, respectively. The resins were washed thoroughly with Milli-Q water after converting the ionic form, so as to remove any entrained solution.

III-C-3. Discussion of Ion-Exchange Results

Presented in Table III-8 are the results of the fixed-bed studies performed employing both strong-base and weak-base resins for

TABLE III-8

CAPACITY AND REGENERABILITY OF VARIOUS ANION-EXCHANGE RESINS FOR THIOCYANATE REMOVAL

Resin	Form	meq SCN^-/cc Resin	Regenerant	% Regeneration
AG1-X8	OH^-	0.97	1 N NaOH	17.9%
		1.03	1 N NH_4OH	0.25%
	HCO_3^-	1.03	1 N NH_4HCO_3	67.%
		1.03	2 N NH_4HCO_3	68.%
AG2-X8	OH^-	0.95	2 N NaOH	65.5%
		1.00	5.6 N NH_4OH	23.6%
	HCO_3^-	1.03	1 N NH_4HCO_3	20.%
MWA-1	Free Base	0.15	2 N NaOH	19.0%
		0.21	5.6 N NH_4OH	7.0%
	HCl	0.89	2 N NaOH	79.6%
A-340	Free Base	0.21	2 N NaOH	73. %
		0.21	5.6N NH_4OH	46. %
	HCl	0.86	2 N NaOH	84.4%
WGR	Free Base	0.15	2 N NaOH	19.0%
		0.21	5.6 N NH_4OH	7.0%
WGR-2	Free Base	0.24	2 N NaOH	81.0%
		0.30	5.6 N NH_4OH	18.0%

thiocyanate removal. Two strong-base (quaternary amine) resins were studied, AG1-X8 and AG2-X8 (both from Bio-Rad Laboratories). In addition, data for four weak-base (tertiary amine) resins, Dowex WGR, Dowex WGR-2, Dowex MWA-1 (Dow Chemical), and Duolite A-340 (Diamond Shamrock), were also obtained.

III-C-3a. Strong-Base Resins

As indicated in Table III-8, the strong-base resins exhibit a higher capacity for thiocyanate than do the weak-base resins. Both AG1-X8 and AG2-X8 demonstrate about the same capacity; however, the two resins differ in their regeneration behavior. Table III-7 demonstrates that AG2-X8 generally exhibits less selectivity for anions relative to OH^- than does AG1-X8; however, the source used for Table III-7 does not report selectivity of the resins for thiocyanate.

Gregor et. al. (1955) have measured the selectivity coefficient (Equation III-13) of thiocyanate with respect to chloride as a function of chloride composition on Dowex 2-X8 resin (Equivalent to AG2-X8). The relative selectivities of anions in Table III-7 were determined by displacing the anions with OH^-, and therefore correspond to relative selectivities of the anions with respect to hydroxide ions over a range of OH^- concentrations on the resin. Since the selectivity coefficient of thiocyanate to chloride was found by Gregor et. al. to be highest at the lowest chloride concentration on the resin, the selectivity coefficient at low Cl^- concentration ($K_{zx} = 12$) could be equated to the ratio of the relative selectivity of SCN^- to OH^-, to that of Cl^- to OH^-. This ratio can then be multiplied by the relative selectivity of Cl^- to OH^- from Table III-7 to yield an estimate of the selectivity of

SCN^- with respect to OH^-. Performing the calculation results in a selectivity of SCN^- to OH^- of 28 ,near the selectivity exhibited by the phenolate ion in Table III- 7. A selectivity of SCN^- to HCO_3- could then be calculated to be about 23. Approximating the selectivity of SCN^- on AG1-X8 as that exhibited by phenolate ion yields selectivities for the AG1-X8 of 74 and 12.3, for SCN^- to OH^- and SCN^- to HCO_3^-, respectively.

The selectivities estimated above explain why AG2-X8 is regenerated better by NaOH than is AG1-X8, and why AG1-X8 is regenerated better by HCO_3^- than is AG2-X8. AG1-X8 displays a higher selectivity for SCN^- over OH^- than AG2-X8 (74 compared to 28), and hence is not regenerated easily by NaOH. On the other hand, AG2-X8 displays a higher selectivity for SCN^- over HCO_3^- (23 compared to 12.3), thereby explaining why HCO_3^- achieved the better regeneration for AG2-X8. In both cases, NH_4OH provided much poorer regeneration than NaOH, owing to the lower basicity of the NH_4OH solution compared to NaOH.

Poor regenerabilities of AG1-X8 and AG2-X8 were obtained despite the large quantities of regenerant used (i.e., 50 bed volumes). Therefore, regeneration of these resins by either NaOH, NH_4OH, or NH_4HCO_3 is not a practical alternative. Regeneration would have to be accomplished with an anion that has a higher affinity for the resins, such as chloride. Whatever regenerant is used must maintain low chemicals cost and yet be acceptable in the process effluent.

III-C-3b. Weak-Base Resins

The data in Table III-8 demonstrate a low thiocyanate capacity for weak-base resins which are in the free-base form. The capacity of a weak-base resin is greatly increased when the resin is first converted to an ion-pair form before use. This effect is illustrated by the higher reported capacities for MWA-1 and A-340 resins that were washed with HCl prior to use, compared to the capacities of the same resins in the free-base form. In the free-base form, the resin can remove HSCN only until the pH of the aqueous phase nears the pK_a of the resin. Any further removal of HSCN increases the pH of the solution to the point that ion-exchange sites are removed by acid dissociation. The ion-pair forms of the resins do not have this limitation, since removal of thiocyanate does not require removal of an hydrogen ion, and the pH does not change with anion exchange.

The ion-pair forms of these resins demonstrated a greater regenerability with NaOH than did the strong-base resins. As discussed above, at pH values greater than pK_a of the resin, the ion-pair form of the resin is less favored than the free-base form of the resin. Therefore, the ion-paired resin will demonstrate a greater regenerability at high pH due to complete removal of the ion-pair, rather than ion exchange. Use of NaOH for regeneration would require the resin to be reconverted to its ion-pair form after regeneration and before reuse. Such a scheme would have a large chemicals consumption associated with both the recovery of thiocyanate and for conversion of the resin back to the ion-pair form. As with the strong-base resin, the weak-base resins were not as fully regenerated by NH_4OH as NaOH, due to the lower basicity of NH_4OH compared to NaOH.

Based on the theory presented above and the results for the strong-base resins, it seems likely that ammonium bicarbonate may be an alternative regenerant for the weak-base resins. The pK_a values of weak-base resins have been found to be in the range 7.6 to 11.1 (Clifford and Weber, 1983). A 0.1 N NH_4HCO_3 solution has a measured pH of 7.8 at 25 C (Windholz, 1983). Therefore, NH_4HCO_3 as a regenerant may permit regeneration of a weak-base resin, without removal of the ion-pair, for a resin with a pK_a greater then 9. Two possible resins for such an application may be Doulite ES-374 (Diamond Shamrock) and Amberlite IRA-68 (Rohm & Haas) which have pK_a values of 9.9 and 11.1, respectively, as determined by Clifford and Weber (1983).

III-D. Stripping

The vapor-liquid equilibrium behavior of a solute in water can be described by equating the liquid and vapor fugacities of the solute to yield the expression:

$$K = y_i/x_i = \gamma_i P_i^{sat}/\ \phi_i P \qquad \text{(Eq. III-20)}$$

where γ is the liquid-phase activity coefficient, x is the liquid-phase mole fraction, P^{sat} is the saturation pressure at the specified temperature, y is the vapor-phase mole fraction, ϕ is the vapor-phase fugacity coefficient, and P is the total pressure. The subscript i denotes the compound of interest. Unless operation is at high pressures, the vapor-phase fugacity coefficient is typically unity, as will be assumed here. Rewriting the above relationship for another component, j, and combining the expressions leads to an expression for the relative volatility of i with respect to j, α_{ij}:

$$\alpha_{ij} = (y_i/x_i)/(y_2/x_2) = \phi_i P_i^{sat}/\ \phi_2 P_2^{sat} \qquad \text{(Eq. III-21)}$$

If component 2 is water (w) , the relative volatility of a dilute solute (s) in water becomes:

$$\alpha_{sw} = \gamma_s P_s^{sat} / P_w^{sat} \qquad \text{(Eq. III-22)}$$

where water is present in excess and its activity coefficient is taken as unity.

Equation III-22 can be used to assess the feasibility of using stripping for the removal of solutes from the condensate water. Solutes that demonstrate large relative volatilities compared to water are easily removed by stripping. Conversely, solutes that demonstrate relative volatilities with respect to water near 1, or below 1, are not easily removed.

Organic solutes in water often demonstrate large activity coefficients and therefore display relative volatilities much greater than would be expected based solely on the vapor pressure of the solute. As presented by Equation III-6 , the aqueous-phase activity coefficient of an organic solute can be obtained with good accuracy from the solubility of the solute in water, for solutes with a mutual solubility with water less than about 1 mole %.

Presented in Table III-9 are the calculated relative volatilities of some of the condensate-water solutes in water, at 100 C and infinite solute dilution. The conditions for which the data were calculated are what would be encountered during atmospheric steam stripping of the solutes from the condensate water. For steam stripping, the vapor phase is essentially all water and the value of α_{sw} becomes the same as

TABLE III-9

RELATIVE VOLATILITY OF VARIOUS CONDENSATE-WATER SOLUTES WITH RESPECT TO WATER, AT INFINITE DILUTION AND 100 C

Solute	γ^{inf}	P_i^{sat}(mmHg)	$\alpha_{iw} = \gamma_i^{inf} P_i^{sat} / P_w^{sat}$
Acetone	9.01	2690.	31.9
Acetonitrile	9.58	1420.	17.9
Methanol	1.66	2740.	6.0
o-cresol	80.1	30.1	3.17
2,3 xylenol	150.	11.1	2.2
2,4 xylenol	110.	15.1	2.2
3,5 xylenol	190.	8.6	2.2
p-cresol	85.6	16.6	1.87
m-cresol	77.7	17.4	1.78
Phenol	31.0	35.6	1.45
Catechol	1.7	4.2	0.009
Hydroquinone	3.2	0.22	0.0009
Resorcinol	0.7	0.65	0.0006

γ^{inf} = Infinite Dilution Activity Coefficient at Stated Temperature
P^{sat} = Saturation Pressure of Solute at Stated Temperature
P^{w} = Water Saturation Pressure at Stated Temperature

K. The procedures used to estimate the values in Table III-9 are summarized in Appendix H.

The data demonstrate that the hydroxybenzenes, although higher boiling than water, exhibit separation factors greater than 1 at low solute concentration. Nevertheless, in order to attain a stripping factor (K/L) of 1.4 or better, the stripper would have to operate with a near equal molar vapor-to-liquid ratio (V/L), resulting in an overhead product of essentially the same composition as the condensate water. To be attractive for stripping, substances should provide values of K two to three orders of magnitude greater than those of the hydroxybenzenes, if the solutes are to be put into a concentrated form. The dihydroxybenzenes have extremely low volatilities and would not be removed from water even at extreme vapor-to-liquid ratios.

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CHAPTER IV

TREATMENT OF CONDENSATE WATER

IV-A. Removal of Organics

IV-A-1. Solvent Extraction

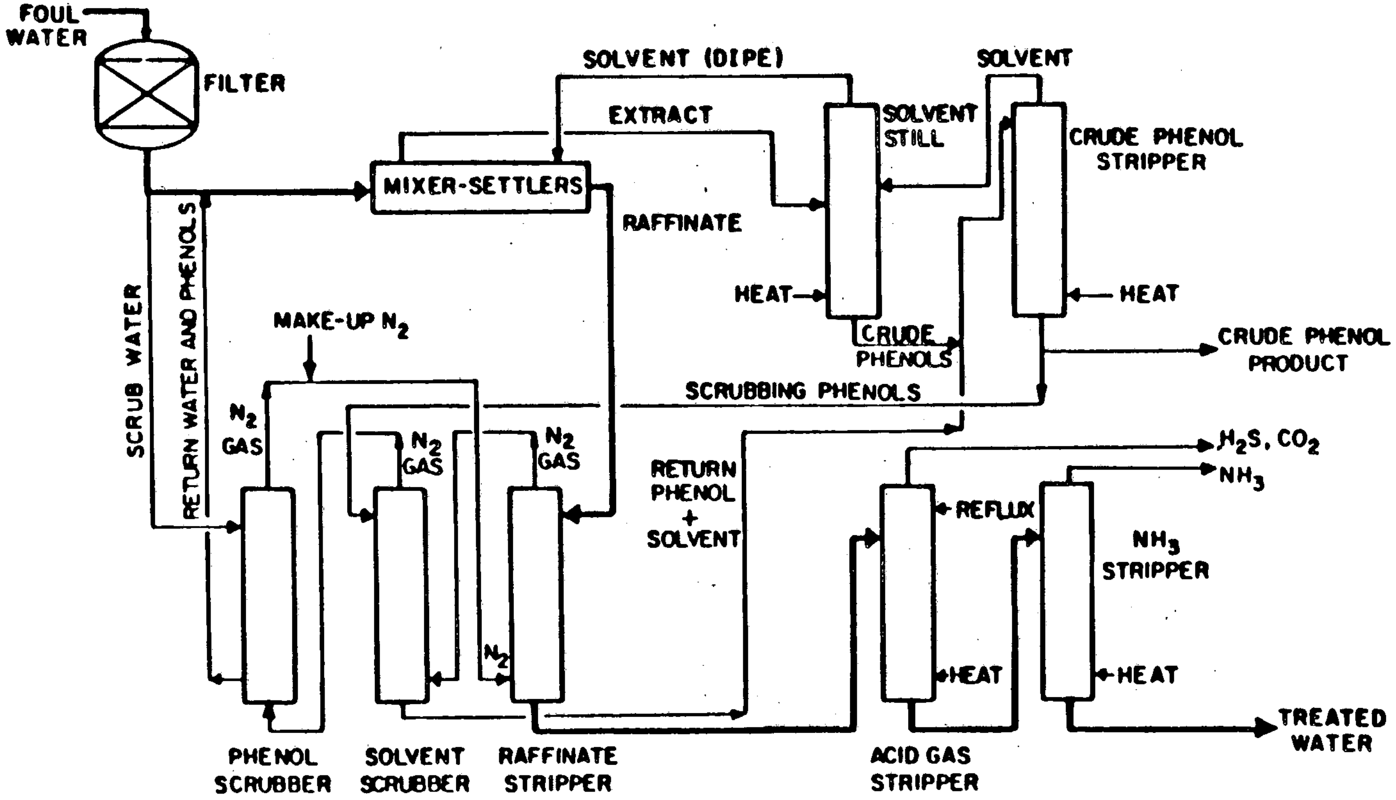
Solvent extraction is a proven method for the removal of phenolic compounds from water. Wurm (1968) traces the history of phenol removal from condensate waters. The removal of phenolic compounds from water first arose in connection with treatment of coke oven wastewaters. The first treatment process introduced for these waters utilized extraction into benzene, with benzene being regenerated via back extraction into sodium hydroxide solution. Later investigations led to the development of the Lurgi Phenosolvan process, which utilized butyl acetate as a solvent. The current version of this process employs diisopropyl ether (DIPE) as the extraction solvent. As mentioned in Chapter I, the Lurgi Phenosolvan process is currently used to treat condensate produced from the Lurgi Gasifiers at Sasolburg, South Africa.

IV-A-1a. Phenosolvan Process

Figure IV-1 presents a process flow diagram for the Phenosolvan process, including additional stripping columns for the removal of acid gases and ammonia. As indicated in Figure IV-1, the incoming water is first extracted with DIPE and then subsequently nitrogen stripped to remove and recover residual solvent. Regeneration of the DIPE is accomplished via distillation, where the DIPE is taken as the overhead product, and the phenol is concentrated in the bottoms product. The

FIGURE IV-1

PHENOSOLVAN PROCESS FLOW DIAGRAM INCLUDING AMMONIA AND ACID GAS STRIPPING (Adapted from Wurm, 1968)



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bottoms product is then further stripped to recover the DIPE and yield crude phenol product.

A unique feature of this process is the use of a recycled nitrogen stream to enable solvent recovery from the raffinate. The DIPE is recovered from the nitrogen stream exiting the raffinate stripper through contact with a portion of the crude phenol product in the solvent scrubber. Finally, the nitrogen exiting from the solvent scrubber is contacted with a portion of the incoming wastewater in the phenol scrubber which serves to absorb phenol from the nitrogen, thereby allowing the nitrogen to be recycled back to the raffinate stripper.

Wohler (1979) presents a description of the Phenosolvan process along with the relative merits of using DIPE versus butyl acetate in the process. DIPE is reported to yield a lower distribution coefficient for phenol than butyl acetate (i.e., K_d(DIPE) = 20 and K_d(Butyl acetate) = 50, both near 40 C, Wohler, 1979); however, this disadvantage is reported to be outweighed by (1) the increased chemical stability and thermal stability of DIPE over butyl acetate, (2) the lower boiling point of DIPE (b.p. 68 C) compared to butyl acetate (b.p. 125 C), and (3) lower solvent losses of DIPE (20 g/m^3 condensate) than butyl acetate (150 g/m^3 condensate). Although ethers can form explosive peroxides upon aging, DIPE is stable in this process due to the presence of the phenolics which act as inhibitors to free radical formation.

Wohler also presents a process flow diagram for the Phenosolvan process that differs slightly from that in Figure IV-1. The process described by that author does not provide the phenol scrubber tower for absorbing the phenol from the nitrogen recycle stream with wastewater. In the design presented by Wohler, the nitrogen stream is sent directly back to the raffinate stripper after contacting the crude phenol product. Since the nitrogen leaving the solvent absorber is saturated with phenol, such a modification should increase the amount of phenol recycled to the solvent stripper, and therefore increase the amount of phenol in the effluent water. Nevertheless, Wohler reports that the process yields essentially complete removal of the hydroxybenzenes. However, it removes only 70% of the dihydroxybenzenes.

IV-A-1b. Chem-Pro Process

A competitive process to the Phenosolvan process is currently licensed by the Chem-Pro Corporation. The Chem-Pro process is reported to utilize methyl isobutyl ketone (MIBK) as an extraction solvent (Scheibel, 1978), with solvent recovery for this process being accomplished via atmospheric steam stripping. MIBK yields higher distribution coefficients than DIPE for extraction of both the hydroxybenezenes and dihydroxybenzenes (see Chapter III); therefore, use of MIBK should enable a high recovery of the dihydroxybenzenes at a reasonably low solvent-to-water ratio.

Greminger et. al. (1982) present an economic analysis for using MIBK to treat condensate water. Their analysis revealed that vacuum-steam stripping was more economical for the recovery of MIBK from the raffinate than atmospheric steam stripping. Vacuum steam stripping was shown to provide lower energy costs and to reduce the capital costs associated with heat exchange equipment. These benefits were found to outweigh the additional costs associated with vacuum operation.

IV-A-1c. Alternatives

i. High-Boiling Solvents

In both the Phenosolvan and the Chem-Pro processes, extraction is performed with a low-boiling solvent, that is, a solvent lower boiling than the extracted solutes, thereby allowing the solvent to be taken overhead in a distillative regeneration column. Both of these processes have a large energy consumption arising from the need to volatilize all the solvent in the distillation column. An energy-saving alternative to these designs would be to employ a solvent which boils higher than some or all of the extracted solutes, thereby allowing the solvent to be recovered in the bottom of the distillative regeneration column. Lower vapor flow rates would be needed in the distillation tower and the distillation tower and its associated condenser and reboiler can be downsized. A high-boiling solvent may require the use of higher pressure steam for the reboiler; however, any additional cost for the high pressure steam should be more than offset though by the substantial decrease in steam consumption. Regardless, vacuum distillation could be employed to lower the reboiler temperature and make use of lower pressure steam.

One reported use of a high-boiling solvent for treatment of condensate waters is that employed by IG Farbenindustrie in the 1930's (Wurm, 1968; Tupholme, 1933). At least two treatment plants in Germany utilized tricresyl phosphate (TCP) as an extraction solvent with solvent regeneration of the TCP being accomplished via vacuum distillation. Tupholme (1933) presents a comparison of the use of TCP versus benzene for extraction of phenols from condensate water and reports that TCP was found to yield higher recoveries of the phenols than did benzene. The higher extractability of phenols from water by TCP can be attributed to the stronger basicity of TCP, as compared with benzene. Bell (1980) reports a weight-fraction-based equilibrium distribution coefficient (K_d) of 72 for extraction of phenol into TCP from water. Although TCP was effective for extraction of phenols from water, Tupholme reports that regeneration of TCP by atmospheric distillation was found to yield a regenerated TCP product that was darkened and more viscous, the changes being attributed to thermal decomposition of the TCP and build up of heavy solutes. Vacuum distillation (12 mmHg absolute and 160 C) was found to avoid thermal decomposition; however, a slight increase in viscosity was observed due to the build up of nonvolatile solutes.

Bell (1980) has investigated the use of other high-boiling Lewis-base solvents, besides TCP, for the extraction of phenol from water. Distribution coefficients of phenol into both Alamine 336 (a commercial tertiary amine) and tri-n-octyl phosphine oxide (TOPO) were determined. Alamine 336 was found to yield relatively low distribution coefficients for phenol ($K_d < 6$) when the amine was dissolved in various diluents. A TOPO-diisobutyl ketone (DIBK) mixture was found to yield large distribution coefficients (i.e., $K_d > 100$) for extraction of phenol.

MacGlashan et. al. (1985) investigated the use of TOPO for extraction of phenolics (i.e., hydroxybenzenes, dihydroxybenzenes, and trihydroxybenzenes) from water into TOPO-DIBK mixtures and presented a chemical model for the extraction mechanism. Distribution coefficients (K_d) greater than 800 were observed in some cases for the extraction of phenol from water. The distillative regeneration of TOPO-diluent mixtures was studied and found to be a feasible alternative for regeneration of TOPO-diluent mixtures after the extraction of phenol.

The condensate waters contain large amounts of dissolved ammonia and acid gases which form buffer solutions with a pH in the range of about 8 to 9. One roadblock to using TOPO for treatment of condensate waters is its tendency to form emulsions with basic solutions. TOPO-DIBK mixtures are reported to form emulsions when washed with greater than 0.001 N KOH solution (Bell, 1982). In this work, a TOPO-DIBK mixture was found to form emulsions when contacted with an aqueous ammonia solution at a concentration greater than 0.001 N.

Table IV-1 presents the boiling points of selected condensate water solutes and various high-boiling and low-boiling solvents. TCP is extremely nonvolatile and is much higher boiling than any of the solutes listed in Table IV-1; however, small amounts of high-molecular-weight acids (e.g tar acids) have also been identified in condensate waters. One possibile regeneration scheme for TCP and other high-boiling bases may be to use vacuum distillation followed by back extraction into aqueous base.

Tributyl phosphate (TBP) is a stronger base than TCP and exhibits very high values of K_d for the condensate water solutes. TBP has seen much application for nuclear fuel reprocessing. The properties and uses of TBP have been recently summarized by Schulz and Navratil (1984). A 50 wt% mixture of TBP in dodecanol was found to yield $K_d > 200$ for the extraction of phenol from water (Chapter III). TBP has a volatility lower than those of the hydroxybenzenes and similar to those exhibited by the dihydroxybenzenes. Distillative regeneration of TBP would not remove the dihydroxybenzenes, or any other high-boiling solutes, from the solvent and would eventually lead to the same problems encountered

TABLE IV-I

BOILING POINTS OF SELECTED CONDENSATE WATER SOLUTES AND VARIOUS HIGH-BOILING AND LOW-BOILING SOLVENTS

Solvent/Solute	Boiling Point (C)
Low-Boiling Solvents:	
Diisopropyl Ether (DIPE)[1]	69.
Butyl Acetate[1]	125.
Methyl Isobutyl Ketone (MIBK)	116.8
Condensate Solutes:	
Phenol[1]	181.4
o-Cresol[1]	190.8
m-Cresol[1]	202.8
p-Cresol[1]	202.
2,3 Xylenol[2]	218.
2,4 Xylenol[2]	210.
2,5 Xylenol[2]	211.5
2,6 Xylenol[2]	212.
3,4 Xylenol[2]	225.
3,5 Xylenol[2]	219.5 (Sublimes)
Catechol[1]	245.
Resorcinol[1]	280.
Hydroquinone[1]	285.
High-Boiling Solvents:	
Tributyl Phosphate (TBP)[2]	289.
Tricresyl Phosphate (TCP)[2]	410.

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(1) Data taken from Perry and Green (1984).

(2) Data taken from Weast (1984).

by TCP. However, TBP could also be regenerated by a combination of vacuum distillation followed by back extraction of the high-boiling solutes into base. Chemical costs for the base would be minimized since only a very small fraction of the solutes have boiling points similar to or higher than TBP. This scheme presents several potential problems which may be overcome by judicious choice of a diluent for the TBP.

One problem is that of potential thermal degradation of the solvent during distillative regeneration. Shoun and Thompson (1984) present reaction rate constants for the thermal decomposition of TBP in presence of oxygen. The thermal decomposition was modeled by first order kinetics (1st order in TBP concentration) and found to demonstrate an apparent activation energy of 40 kcal/mol. Using their data, an estimate of TBP degradation that would occur upon distillative regeneration at various temperatures was calculated based on the following assumptions: (1) pure TBP solvent at solvent-to-water ratio of 0.1 for the extraction, (2) an average hold-up time of 15 min in the distillation column, and a TBP price of \$1.60/lb (Chemical Marketing Reporter, 1984). The calculations indicated that TBP losses via decomposition would amount to \$1.10/1000 gallons condensate water at 260 C; however, the TBP losses would be almost negligible, <\$0.01/1000 gallons condensate water, at 140 C. Although these estimates are not highly precise, the relative decomposition rates indicate that vacuum distillation is a necessary alternative to atmospheric distillation for TBP regeneration.

The above reasoning is based on the thermal degradation of TBP in presence of oxygen. If oxygen could be excluded from the system, the rate of thermal degradation of TBP may be low enough to allow use of atmospheric distillation for regeneration.

Another obstacle to the use of TBP is the possibility of decomposition of the TBP upon contact with an aqueous base. Shoun and Thompson present decomposition rate parameters for contacting 20 vol% TBP in kerosene with 1 M NaOH at 30 C and 50 C. The rate constants for hydrolysis by base at 30 C are of the same order as the thermal decomposition rate constants at 260 C, mentioned above. The reaction of TBP with NaOH was found to be near first order in both TBP and OH- concentrations. However, the hydrolysis is reported to occur only in the aqueous phase and is therefore limited by the solubility of TBP in the alkaline medium. As discussed in Chapter III, the proper choice of a diluent for TBP can greatly reduce the aqueous solubility of TBP. Despite the reported tendency of TBP to be hydroyzed by base, aqueous Na_2CO_3 solutions have been successfully used for the recovery of fission products from TBP in the Purex process, and no decomposition of TBP has been reported. Aqueous solutions of Na_2CO_3 have a measured pH of near 11.6 (Windholz, 1983).

Ammonia is the cheapest base (per mole of basicity) available and is also a product of condensate water treatment. As discussed in Chapter III, ammonium hydroxide can be used effectively for the back extraction of phenolic compounds from a solvent, provided that the distribution coefficients of the solutes of interest are not too large (i.e., K_d values of perhaps 10 to 20). With proper choice of the concentration of TBP in the solvent phase and the proper diluent, a TBP-diluent mixture can be obtained which would yield distribution coefficients in that range for extraction of the dihydroxybenzenes from condensate water. Back extraction of the dihydroxybenzenes into aqueous ammonia could then be carried out. The use of such a diluent (e.g., an alcohol) to yield a favorable K_d has the added benefit of lower solubility of TBP in the aqueous phase, because the diluent reduces the activity coefficient of TBP in the aqueous phase. In addition, a 1M NH_4OH solution has a measured pH of 11.6, equal to that of Na_2CO_3 solution; therefore, no hydrolysis of TBP should occur. The hydroxybenzenes display much larger distribution coefficients than the dihydroxybenzenes; however, the hydroxybenzenes can be recovered from the TBP solvent by vacuum distillation at a temperature low enough to avoid appreciable thermal decomposition of TBP. Such a process is illustrated in Figure IV-2.

The processing scheme presented in Figure IV-2 should be able to provide essentially complete removal of the hydroxybenzenes and dihydroxybenzenes from the condensate water. The equilbrium distribution coefficients of 5,5-DMH and thiocyanate into TBP were determined to be 2.2 and 0.7, respectively; therefore, the raffinate leaving the extractor would still contain small amounts these solutes. The raffinate leaving the extractor would also be saturated by the TBP-diluent mixture. The factors affecting solvent recovery are discussed below.

ii. Solvent Recovery

A large cost which can be associated with solvent extraction processes is that of lost solvent. Both the Phenosolvan and the Chem-Pro processes utilize stripping of the raffinate to recover dissolved solvent. Presented in Table IV-2 are the costs and water solubilities of various solvents as reported by King and Senetar (1986). The costs

FIGURE IV-2

EXTRACTION WITH A HIGH-BOILING SOLVENT WITH SOLVENT REGENERATION BY VACUUM DISTILLATION AND BACK EXTRACTION INTO AMMONIA

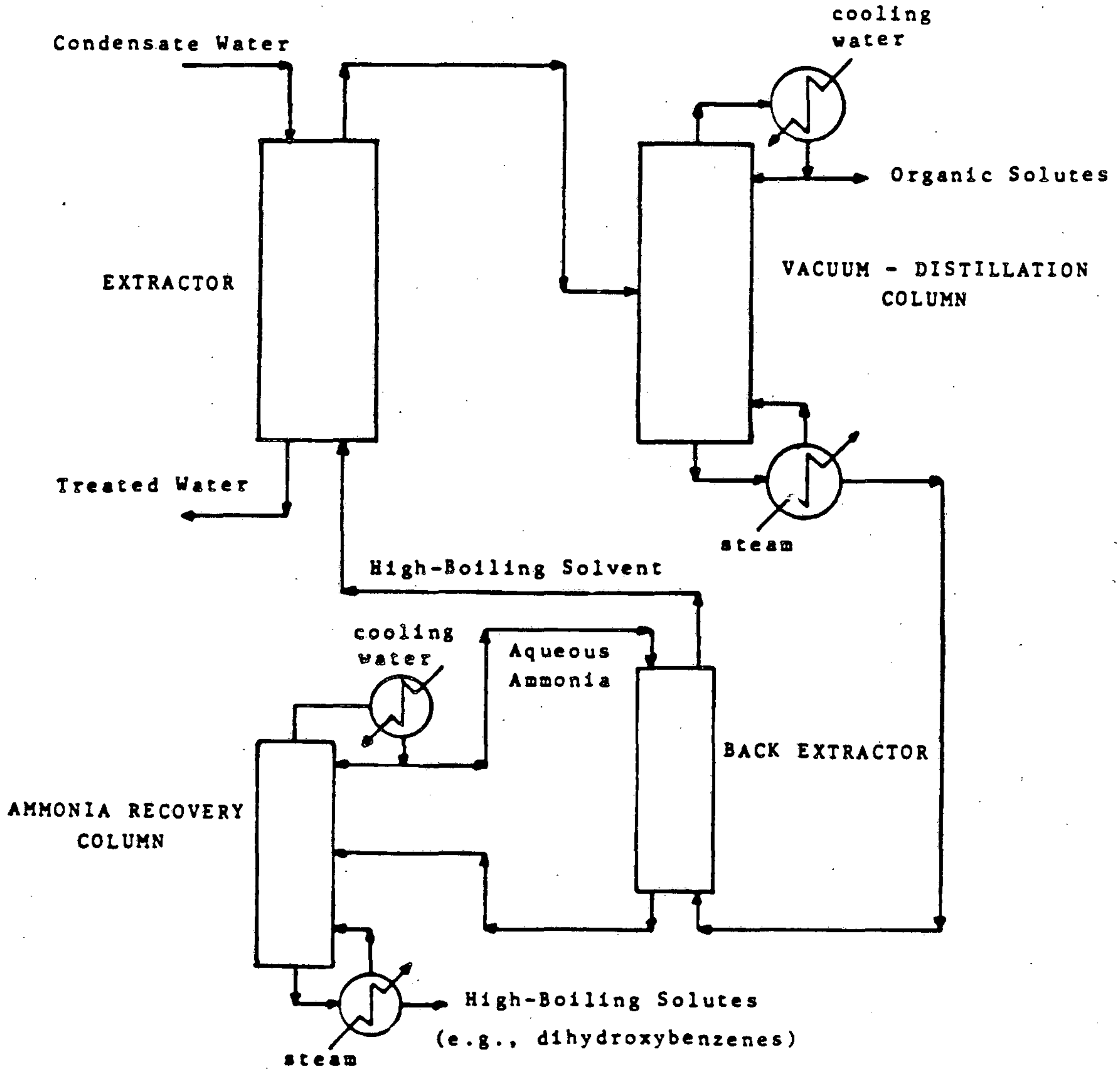

TABLE IV-2

COST AND WATER SOLUBILITY OF VARIOUS SOLVENTS

Solvent*	Price ($/kg)	Solubiluty in water (wt%)	Cost of Solvent Leaving Extractor with Raffinate ($/cubic meter water)
Kerosene	0.39	----	----
Toluene	0.40	0.05	0.20
DIPE	0.82	0.20	1.64
MIBK	1.08	1.90	20.92
IBHK	1.08	>0.01	>0.11
1-Octanol	1.54	>0.01	>0.15
DIBK	1.32	0.05	0.66
Alamine 336	3.15	>0.001	>0.03
TBP	3.64	0.042	1.53
TOPO	14.88	>0.0001	>0.015

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*DIBK = Di-isobutyl ketone
DIPE = Di-isopropyl ether
IBHK = Isobutyl heptyl ketone
MIBK = Methyl isobutyl ketone
TBP = Tributyl phosphate
TOPO = Trioctyl phosphine oxide

Source: King and Senetar (1986)

are based on December 1984 solvent prices. Also presented in Table IV-2 are the resulting costs ($/m^3 water) of the solvents leaving the extractor with the raffinate. The data demonstrate that in most cases there is a substantial economic incentive for solvent recovery. The costs reported in Table IV-2 do not reflect any additional losses which may occur through entrainment and/or transients. Entrainment results in higher treatment costs, and is a greater consideration for the more expensive solvents.

Although a high-boiling solvent such as TBP has a low water solubility, its high cost requires solvent recovery from the raffinate and/or a reduction in the extent that TBP partitions into the raffinate. The data presented in Table IV-2 are for pure TBP and not a TBP-diluent mixture. As discussed in Chapter III, the solubility losses of TBP in water can be reduced by lessening the activity of TBP in the solvent phase through proper choice of a diluent and varying the concentration of TBP. Aqueous losses of TBP are typically decreased by diluents with greater polarity. On the other hand, some of the more acidic diluents interact with the basic phosphoryl group on the TBP and lessen its ability to extract. Nevertheless, as demonstrated in Chapter III, a solvent mixture of 50 wt% TBP in dodecanol was found to yield distribution coeffiecients for the dihydroxybenzenes larger than required for back extraction into ammonia. Data presented by Burger (1984), for 10 vol % TBP in various diluents, demonstrate that the TBP solubility in water can be reduced from near 0.3 g/L to below 0.02 g/L, by switching from a kerosene diluent to a benzene diluent. A diluent such as dodecanol is more acidic than benzene and would be expected to yield a TBP loss lower than that with benzene. The solubility of dodecanol in water should be small.

In addition to providing a favorable K_d and controlling solvent losses, diluents are also chosen to control other properties such as the boiling point, density, and viscosity of the solvent phase. Some extractants are extremely nonvolatile or tend to decompose at high temperatures. When distillative regeneration is to be used for a high-boiling extractant, a favorable diluent may have a boiling point significantly higher then that of the solutes, but lower than that of the extractant, thereby decreasing the necessary reboiler temperature. Dodecanol (b.p. 255-259 C) was choosen as a likely diluent for TBP (b.p. 289 C) in that dodecanol is significantly less volatile than the highest boiling hydroxybenzene solute (3,4 xylenol, b.p. 225 C), yet dodecanol has a higher volatility than TBP.

Dodecanol also has a favorable density (0.831 g/cm^3) compared to those of TBP (0.976 g/cm^3) and water (1 g/cm^3), thereby permitting greater ease in phase separation of the solvent mixture from water. The viscosity of dodecanol is expected to be rather large near ambient temperature and therefore an additional diluent may be necessary to obtain a lower viscosity. One such diluent would be hexadecane, which has a viscosity of 0.92 cp at 20 C and a boiling point of 254 C. Since regeneration would occur at elevated temperatures, high viscosity is not likely to be a problem in the regeneration.

IV-A-2. Adsorption

Adsorption of organic solutes from water onto either activated carbon or polymeric resins has been shown to be an effective means of achieving low effluent levels of adsorbable organic solutes. The relative advantages and disadvantages of using adsorption as a method for treatment of condensate water have been discussed in Chapter I.

IV-A-2a. Activated Carbon

The data presented in Chapter III reconfirm that phenolic compounds are adsorbed onto activated carbon to a high degree, and that regeneration of activated carbons is not easily accomplished. In addition, activated carbon was found to remove 5,5-dimethyl hydantoin (5,5-DMH) effectively from water and to allow recovery of 5,5-DMH by solvent regeneration with methanol. Solvent regeneration with either methanol or aqueous ammonia was found to be an ineffective means for the removal of phenolics from activated carbon. Thermal regeneration is reported to be an effective means for removal of phenolics, but this also results in a loss of bed capacity in each regeneration cycle.

The use of activated carbon for bulk removal of solutes from the condensate water is limited by the regenerability of activated carbon after adsorbing phenolic compounds. The decrease in bed capacity of activated carbon upon thermal regeneration would have a more profound effect on the economics as the required frequency of regeneration increases. For this reason, use of activated carbon is best suited for removal of trace compounds in the condensate water where bed regeneration would occur much less frequently.

Solvent extraction with MIBK or TBP is capable of removing essentially all the phenolics from the condensate water. If extraction with either MIBK or TBP is employed prior to carbon adsorption, only trace amounts of the phenolics would be left in the raffinate and nonextractable solutes such as 5,5-DMH could be removed by activated carbon. A carbon adsorption bed could be routinely regenerated by solvent leaching; however, periodic thermal regeneration of the bed would be required to avoid the build up of trace phenolics.

IV-A-2b. Synthetic Resins

The results in Chapter III indicated that a synthetic resin such as Amberlite XAD-7 (polyacrylic ester, Rohm and Haas) can effectively adsorb both catechol and 5,5-DMH from water. Solvent regeneration of Amberlite XAD-7 was found to be easily accomplished through the use of either methanol or aqueous ammonia. The capacity for adsorption of catechol and 5,5-DMH from water was not as great as it was using activated carbon; however, the ability to employ solvent regeneration for the recovery of the phenolics is an advantage of the synthetic resin over activated carbon.

As discussed above for solvent extraction, ammonia is a cheap base which is also available as a byproduct from the treatment process. The advantages of using ammonia for regeneration over using an organic solvent are (1) ammonia solution does not need to be rinsed from the column if ammonia stripping occurs downstream and (2) ammonia losses are less costly than solvent losses.

A drawback of using aqueous ammonia is that the solutes may be recovered as ammonium salts and that any unionizable solutes may not be recovered from the resin. There is a possibility of cracking the salts thermally to recover the solutes in their acid forms and to recover ammonia. Residual extraction solvent in the condensate water would probably not be recoverable by ammonia regeneration. The bed would eventually saturate with solvent and require some other form of regeneration, such as solvent regeneration with methanol or acetone.

Fox (1979) presents an economic analysis for using Amberlite XAD-4 (styrene-divinylbenzene resin, Rohm and Haas) for the removal of phenol from water, including regeneration of XAD-4 with either caustic, acetone, or formaldehyde. As expected, the costs reported for the treatment process increase with increasing phenol concentration in the aqueous steam, due to increased frequency of regeneration. The steam consumption for the distillative solvent regeneration was found be a large contributor to the annual operating cost.

Although phenol appears to be able to be removed from XAD-4 easily, the question remains as to whether all the condensate water compounds can be removed as easily as phenol. In the analytical work performed in Chapter II, a bed of XAD-4 was used to fractionate the condensate water. In these experiments, the lead portion of the XAD-4 bed turned dark brown after the bed had been contacted with condensate water. After successive washings with acetone, base, and acid, the resin still retained some brown color, indicating that the desorption had not been complete. The brown-colored solutes were suspected to be oxidation products of the phenolics; however, in an actual process, it may be possible to exclude oxygen, and these products may not form. Further investigation is required as to the regenerability of a polymeric resin, such as XAD-4, after contacting actual condensate waters. The presence of irreversibly adsorbed species would fix the cycle time before disposal or major clean-up of the resin would be necesssary. If the resin could not be effectively regenerated, the cost of replacing the resin may limit the use of adsorption to removal of trace species after bulk removal has been achieved.

IV-A-3. Stripping

As discussed in Chapter III the applicability of stripping organic solutes from these condensate waters is very limited. The low-boiling solutes with high volatility exhibit low enough activity coefficients in water so as to require large amounts of stripping medium. The higher-boiling solutes, although most of them possess much higher activity coefficients in water, have such low volatilities that stripping of these solutes is also not economical.

Stripping is a viable method for solvent recovery. The Phenosolvan process utilizes inert-gas stripping to recover DIPE from the raffinate after extraction. The activity coefficient of DIPE in water at infinite dilution has been reported to be 663 at 100 C (Gmehling et. al., 1981). Using this activity coefficient in Equation III-22 yields a relative volatility of DIPE with respect to water of near 2000, illustrating why stripping is an effective means for recovery of DIPE from the raffinate.

Butyl acetate has a reported activity coefficient of 71.23 at 100 C (Gmehling et. al., 1981) and is less volatile than water (i.e. butyl acetate b.p. = 126.5). As mentioned above, the higher volatility and ease of recovery of DIPE over butyl acetate were the reasons DIPE was used in place of butyl acetate. Gmehling et. al. do not report any activity coefficient data for MIBK in water; however, one would expect that the relative volatility of MIBK to water would be somewhere between that of the relative volatilities demonstrated by DIPE and butyl acetate.

Stripping is typically carried out with steam at atmospheric pressure or under a vacuum, or with an inert gas. Inert gas stripping, as used in the Phenosolvan process, is an economical alternative, provided that the stripped solvent is easily recoverable from the inert gas enabling the inert gas to be recycled. Condensing the solvent from the overhead vapor of an inert-gas stripper could require costly refrigeration; however, other recovery schemes, such as that used by the Phenosolvan process, provide an economical recovery scheme (See Section IV-A-1a).

Steam stripping typically allows solvent recovery from the stripped gases through condensation with cooling water. Atmospheric steam stripping involves a large energy cost associated with raising the temperature of the influent water up to the operating temperature of the stripper (100 C). Vacuum steam stripping can reduce the energy costs by lowering the operating temperature of the stripper down to the temperature of the inlet water. However, the lower energy costs are achieved through an increase in capital costs for the vacuum operation (See Section IV-A-1b).

IV-B. Removal of Inorganics

Ammonia and dissolved acid gases, such as carbon dioxide, comprise the majority of inorganic compounds in the condensate water. These inorganic solutes are often found in sour waters from petroleum refining, and methods for their removal have been developed over the years. Traditional means for treating sour waters have been to strip the dissolved gases from solution. A few of these methods are described briefly below.

In addition to the dissolved carbon dioxide and ammonia, other inorganic solutes are also present. Inorganic species in condensate water include sulfide, cyanide, thiocyanate, and chloride anions, plus cations of trace metals. The trace metals are frequently present in concentrations less then 1 ppm and therefore are not usually a consideration for the treatment processes. Of the inorganic anions, sulfide and cyanide are easily stripped from solution, as hydrogen sulfide and hydrogen cyanide, during removal of the carbon dioxide. However, hydrogen chloride and hydrogen thiocyanate are very strong acids and therefore chloride and thiocyanate cannot be stripped from solution without the addition of acid to bring the solution to a very low pH.

IV-B-1. Stripping

Presented in Figure IV-3a and Figure IV-3b are two processes currently used for the removal of dissolved ammonia and acid gases from water. Figure IV-3a illustrates the CLL (Chemie Linz AG and Lurgi) process as described by Wohler (1979). In this process the condensate is first stripped of the majority of acid gases in the deacidifier, and then sent to the total stripper for removal of the ammonia and the remaining acid gases, primarily carbon dioxide. The overhead product from the total stripper is sent to the CO_2 scrubber for separation of ammonia and CO_2. Part of the overhead vapor from the total stripper is condensed and used as reflux for the total stripper. A product is drawn off near the bottom of the CO_2 scrubber, stripped to remove excess ammonia, and then sent back to the deacidifier as ammonium carbonate solution. The overhead from the CO_2 scrubber is compressed and separated from the volatile organics via distillation to yield a liquid

FIGURE IV-3a

CLL PROCESS (Chemie Linz AG and Lurgi) FOR SEPARATION AND RECOVERY OF AMMONIA AND ACID GASES FROM CONDENSATE WATER (Wohler, 1979)

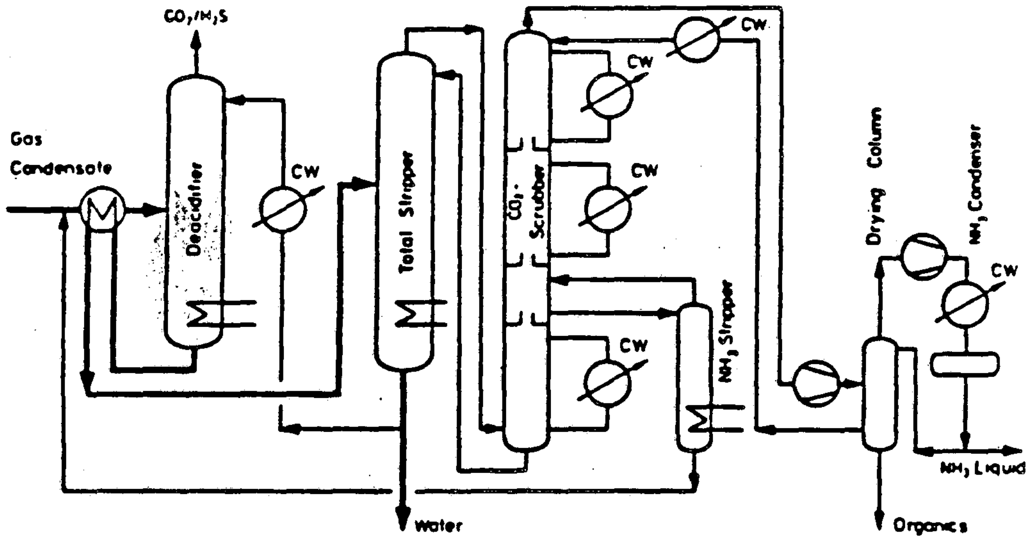
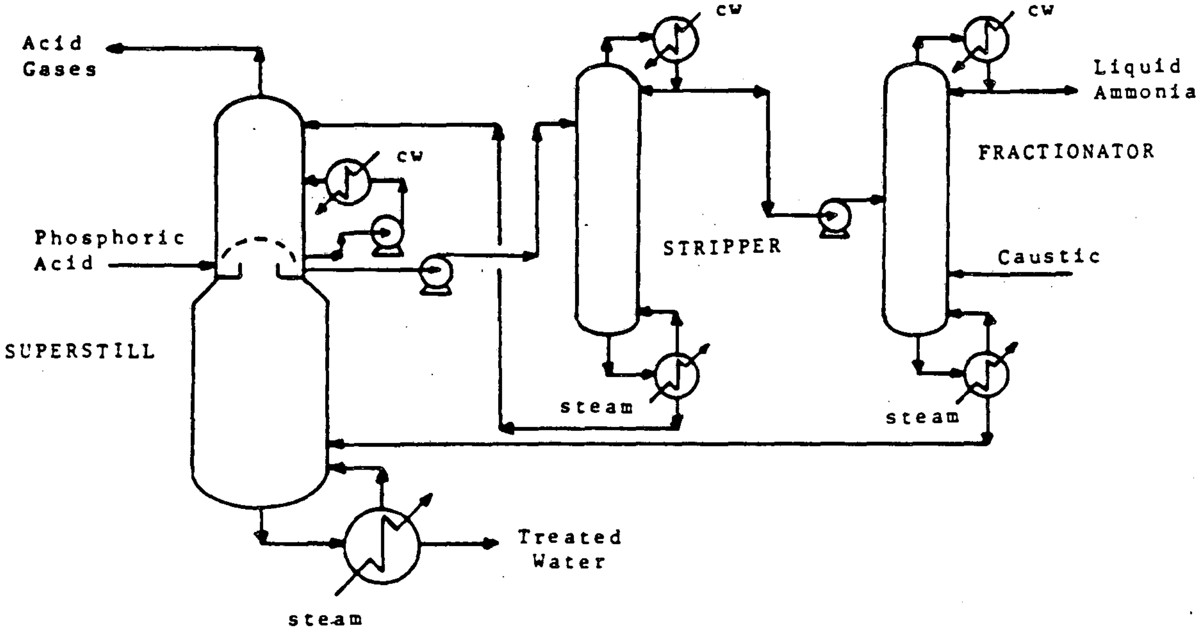


FIGURE IV-3b

PHOSAM-W PROCESS (Adapted from Seufert et. al., 1979)



ammonia product.

The CLL process is reported to recover some low-boiling organic solutes (i.e, acetone, actonitrile, and methanol) from the condensate water. However, based on the relative volatilities presented in Chapter III (Table III-9) for these solutes, it is doubtful that quantitative recovery of these solutes is achieved. Methanol displays a relative volatility with respect to water of about 6.0. The removal of methanol from the condensate water during stripping would require substantial boilup in the CO_2 stripper. However, the boilup in the total stripper and CO_2 scrubber are reported to be large enough to allow complete recovery of residual solvent (i.e., DIPE). Dissociated species such as thiocyanate would not be recovered from the condensate by the CLL process.

The Chevron Wastewater Treating (WWT) process is another sour water treament process related to the CLL process. The WWT process relies on the successive stripping of first the acid gases and then the ammonia from the inlet water. The fate of the organic compounds should be similar to that discussed for the CLL process. A more detailed analysis of the WWT process is presented by Leonard et. al. (1984).

The Phosam-W process (Figure IV-3b) is another method used to remove ammonia and acid gases from sour waters. The working of this process have been recently discussed by Rice and Busa (1984). The diagram shown in Figure IV-3b is that given by Seufert et. al. (1979). In this process the feed water is introduced into the bottom portion of the superstill where both ammonia and the acid gases are stripped together from solution. Treated water is recovered from the bottom of the stripper. The stripped gases are contacted with an aqueous ammonium phosphate solution (NH_3/H_3PO_4 molar ration = 1.2 to 1.4) in the upper portion of the superstill. The ammonium phosphate solution absorbs the ammonia out of the stripped gases, allowing the acid gases to be collected overhead. Ammonia-rich ammonium phosphate solution (NH_3/H_3PO_4 molar ratio = 1.7 to 2.0) is withdrawn from the upper section and stripped to recover the ammonia. The lean ammonium phosphate solution is recycled back to the superstill, and the ammonia (aqueous solution) is distilled in the ammonia fractionator to produce ammonia free-water and anhydrous ammonia. In addition, some phosphoric acid is added to the upper portion of the superstill as make-up.

As is the case for the CLL process, the Phosam-W process may also remove some of the volatile organic solutes from the condensate water, depending on the boil-up in the superstill. These would be recovered with the acid gases. A 0.2 M solution of ammonium phosphate, monobasic ($(NH_4)H_2PO_4$) is reported to have a pH of 4.2 and solutions of ammonium phosphate, diabasic ($(NH_4)_2HPO_4$) are reported to have a pH near 8 (Windholz, 1983). Since hydrogen thiocyanate is a strong acid, it is doubtful that any appreciable amount of thiocyanate would be stripped at the pH of the recycled ammonium phosphate solution.

IV-B-2. Ion-Exchange

IV-B-2a. Anion Exchange

The use of anion exchange for bulk removal of all the acid gas solutes is not likely to be an attractive alternative. Regeneration of anion exchangers is typically accomplished by displacement of the adsorbed anions with anions from a regenerant solution. Hydroxide ion (OH-) would be perhaps the only alternative for regeneration since other anions would tend to be contaminants themselves. The high concentration of anionic species (i.e., dissolved CO_2 as HCO_3^-) in the condensate water would require frequent bed regenerations and large chemicals costs.

For trace removal of the lower-concentration anions from solution, anion exchangers can be economicly attractive. Anion exchange was investigated in Chapter III as a possible means for removal of thiocyanate ion from the condensate waters. As presented in Chapter III, both weak base and strong base resins can effectively remove SCN^- from aqueous solution. Weak base resins offer the possibility of allowing regeneration of the anion- exchange resin with NH_4HCO_3, an inexpensive regenerant and available as a product of condensate treatment. Regeneration with NH_4HCO_3 would put the anion exchanger in the HCO_3^- form; however, for treatment of trace quantities of anions only a small amount of HCO_3^- would be displaced from the resin in relation to the condensate throughput.

In addition to the weak-base resins, liquid amines can also be employed for thiocyanate removal. Amine solvents have the disadvantage of requiring constant replenishment due to solubility and entrainment losses.

IV-B-2b. Cation Exchange

Cation exchangers can provide effective removal of cationic solutes from the condensate water. Ammonium is the principle cation present in the condensate water and is present in large quantities. Bulk removal of ammonia with cation exchange resins suffers from the same limitation as bulk removal of carbon dioxide with anion-exchange resins, in that chemical regeneration techniques result in large chemicals costs. Thermal regeneration is limited by thermal stability of the cation exchange resin; however, strong-acid cation-exchange resins have a operating temperature limit as high as 120 C in the H^+ form (Vermeulen et. al., 1984). Liquid cation exchangers are available that have greater thermal stability. Also, thermal regeneration of liquid cation exchangers does not have the materials handling problems presented by solid resins and would not be as limited by diffusion rates within the polymer.

Mackenzie and King (1985) have introduced a process which employs simultaneous stripping of acid gases and solvent extraction of ammonia, with a liquid cation exchanger, for treating sour waters. They found that di(2-ethyl hexyl) phosphoric acid (D2EHPA) removed ammonium ion satifactorily from the aqueous solution (i.e., exchanging an H^+ ion from D2EHPA for the NH_4^+ ion in the aqueous solution) and lowered the pH of the aqueous solution enough to allow the acid gas solutes to be much more readily stripped. The D2EHPA-ammonium pair was thermally regenerated to liberate ammonia and regenerate D2EHPA. The projected operating cost of the process was found to be higher than that of the Phosam-W process; however, the process should be improved if D2EHPA were replaced with a liquid cation exchanger that was more thermally stable, less water soluble, and/or a somewhat weaker acid.

IV-C. Ordering of Processes

IV-C-1. Stripping vs. Extraction

Based on the above discussion some conclusions may be drawn as to the order in which the condensate water should be processed. Stripping processes have the advantage that if placed after extraction, stripping may serve the duel purpose of recovery of dissolved gases and the recovery of residual solvent from the raffinate, if the solvent can be separated easily from the stripped gases. The combination of solvent recovery with dissolved gas removal is only possible when employing a solvent of relatively high volatility and when the vapor flow requirements for stripping the solvent are not much greater than that required to remove the dissolved gases. Whenever combination of these two processes is feasible, the overall processing costs should decrease.

Waiting to strip the dissolved gases until extraction has been performed should have no adverse effect on the extraction process as long as the pH of the condensate water is not near the pK_a of the solutes being extracted. The pH of the condensate water is set by the relative amounts of dissolved acid gases and ammonia. The more ammonia is in excess of the acid gases, the higher the pH. The phenolics have pK_a values near 10; therefore, for waters of high pH stripping may be necessary before extraction.

If a high-boiling solvent is employed for the extraction, there is no obvious advantage to performing stripping of acid gases after extraction. However, there is an advantage to performing the stripping operation first in that stripping can make use of the sensible heat of the condensate water. After the quench operation, the condensate water is typically cooled before extraction, since lower extraction temperatures usually favor higher distribution coefficients for the solutes in the solvent phase and favor decreased solubility of solvent in the raffinate phase. Extraction at the source temperature may be possible for some of the heavier solvents that are not very water soluble and display large distribution coefficients (i.e., TBP). Since stripping of dissolved gases in both the CLL process and Phosam-W process occurs above atmospheric pressure, much heat transfer is necessary to bring the condensate water up to the temperature of the stripping column. Stripping the condensate water before extraction would decrease the heat exchanger area required to preheat the feed to the stripper. For the process proposed by Mackenzie and King, extraction preceeding the dissolved gas removal would avoid the build up of organic solutes in the cation exchange solvent. However, the coextraction of organics with ammonia could be an advantage if a way were found to fractionate organic solutes from the ammonia during regeneration.

Placement of stripping first may also be favored by a decrease in the formation of hydantoins in the condensate water. As discussed in Chapter II, 5,5-dimethyl hydantoin (5,5-DMH) is suspected to be formed in the condensate water through the reaction of acetone, cyanide, ammonia, and carbon dioxide. Separation of the ammonia from the acid gases would halt the reaction. The Phosam-W process should be very effective at halting the formation of hydantoins in that ammonia is rapidly adsorbed into the acid solution, and the low pH of the absorber solution would not allow a significant amount of the acid gases to be adsorbed into solution. The CLL process should also be effective at decreasing hydantoin formation since cyanide should be removed overhead in the deacidifier column and separated from the remaining reactants.

The above discussion assumes that hydantoins are formed predominately during the treatment of the waters and not during the quenching process. It is likely that hydantoins form chiefly in the quench circuit since the temperature is highest there (i.e., fastest rate of reaction) and the residence time of the water in the quench circuit can be very large. (Recall the METC Run-101 operating data in Chapter I giving a ratio of recycled water to treated water near 700).

IV-C-2. Adsorption

Adsorption is well suited for trace removal of solutes from water after bulk removal has been accomplished by solvent extraction. However, water fed to an adsorption process should have a low amount of dissolved solvent, since any residual solvent in the treated water would greatly increase the frequency of bed regeneration required. This means that a solvent recovery step must be performed prior to adsorption when using solvents such as MIBK and DIPE. As discussed above, solvent recovery may be combined with dissolved gas removal in some cases. High-boiling solvents such as TBP-dodecanol mixtures with low TBP concentration have very low water solubility and low volatility and therefore may be best removed from the treated effluent by adsorption. TBP adsorption and adsorbent regeneration need to be furthur studied.

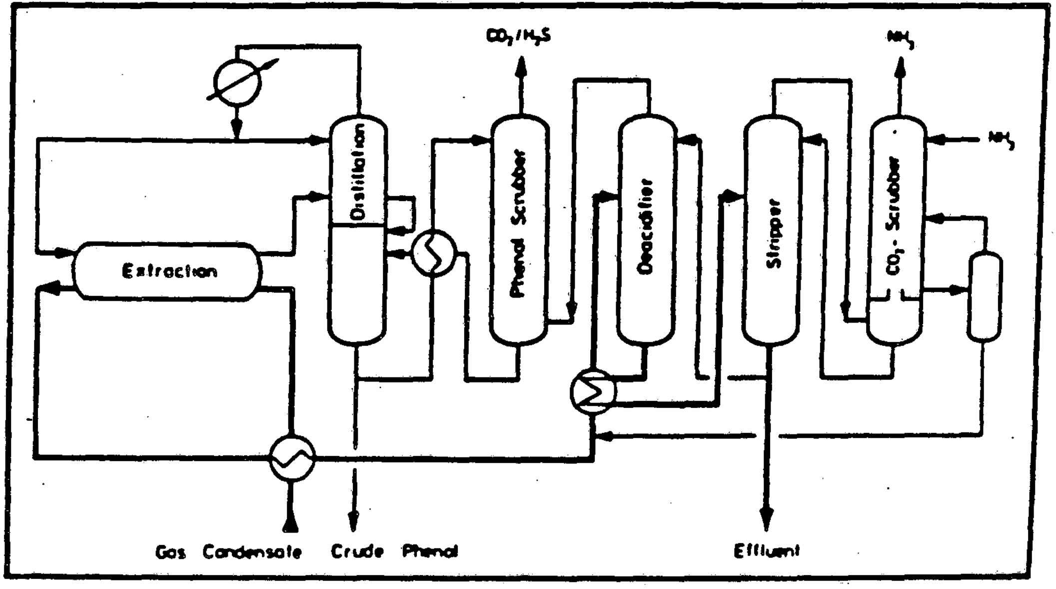
Adsorption should be placed before an ion-exchange processes that employ solid resins since solid ion-exchange resins can be fouled by organic solutes.

IV-D. Integrated Processes

Figure IV-4 presents the combination CLL/Phenosolvan process, as described by Wohler (1979). This process combines the removal of acid gases with the recovery of DIPE, thereby eliminating the nitrogen recycle stream used in the Phenosolvan process. Wohler claims that in

FIGURE IV-4

COMBINED PHENOSOLVAN/CLL PROCESS FOR REMOVAL OF DISSOLVED GASES AND DEPHENOLIZATION OF CONDENSATE WATERS (Wohler, 1979)



such a process DIPE will be removed with the acid gases in the deacidifier column. The acid gases are contacted with some of the phenol product in the phenol scrubber to recover the DIPE from the acid gas stream. It should be noted that the same effect can also be accomplished by feeding the raffinate from the extractor directly to a Phosam-W process, recovering the solvent overhead with the acid gases, and then scrubbing the acid gases with phenol product.

Lienhard and Winkler (1983) report that the condensate treatment process used in Sasol II and Sasol III is the Phenosolvan process followed by the CLL process, with biological treatment as a final treatment step. The effluent is reportedly used as cooling tower make up, and no major problems regarding biofouling and corrosion have been encountered.

IV-E. Opportunities For Improvements

IV-E-1. Two-Stage Versus Single-Stage Quench

Changes in the quench circuit design can lessen condensate treatment costs. The advantages of a two-stage quench over a single-stage quench have been discussed by Parsons (1979) and Wohler (1979). According to Wohler, a 2-stage quench can be operated to provide two condensate water streams of very different composition. The first condensate product would contain the majority of the dissolved gases and the dihydroxybenzenes, while the second condensate product would contain the hydroxybenzenes and the lower boiling solutes and would have less dissolved gases. The first-stage condensate water would be a small fraction of the total condensate and would serve to concentrate the dihydroxbenzenes and the salts. Wohler did not report the relative amounts of the two condensate products; however, Parsons has reported that as little as 10 gallons condensate per ton of coal could serve to remove halides and other strong electrolytes in a first-stage quench. The distribution of compounds in a staged quench needs to be determined.

Presented in Figure IV-5 is a two-stage quench circuit design including solvent extraction of the condensate fractions with DIPE, as described by Wohler (1979). The two-stage quench design allows for using a larger solvent-to-water ratio for the extraction of the first-stage condensate water than is used for extracting the second-stage condensate water, without an increase in total solvent recycle rate compared to the single-stage quench design. This modification allows for essentially complete removal of the dihydroxybenzenes from the condensate water. The dihydroxybenzenes were previously removed to the extent of only 70% in the single-stage quench treatment employing the same total solvent recycle rate. The first-stage quench stream has a smaller flow than the second stage quench stream and has a high concentration of dissolved salts. The second stage condensate water is largely salt-free and therefore does not require as much processing to remove the dissolved salts.

The use of a two-stage quench presents other opportunities for improved treatment schemes. Some of the possible alternatives are listed in Table IV-3.

The first-stage quench water need not be treated in the same manner as the second-stage quench water. Since the first-stage quench contains a high concentration of salts and is obtained at a higher temperature, it would be beneficial first to strip the dissolved gases from solution before removal of the organics, thereby making use of the sensible heat

FIGURE IV-5

ENHANCED REMOVAL OF DIHYDROXYBENZENES THROUGH THE USE OF A TWO-STAGED QUENCH (ADAPTED FROM WOHLER, 1979)

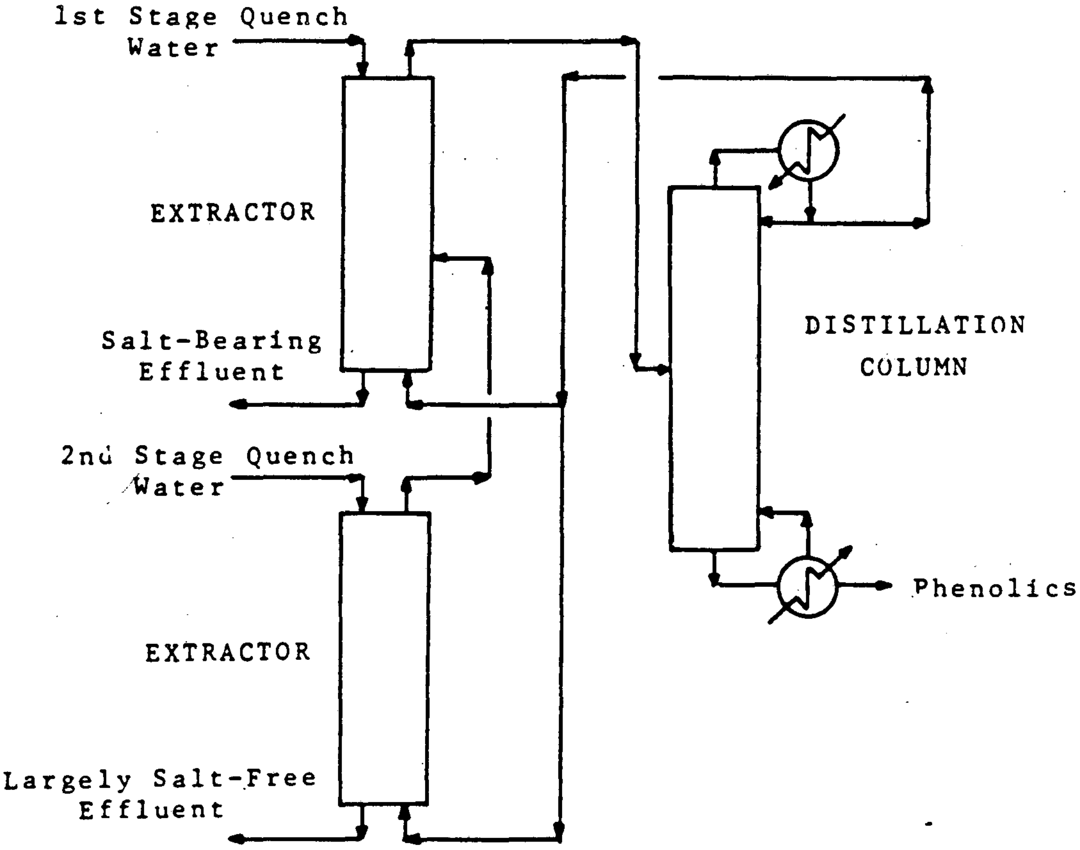


TABLE IV-3

ALTERNATIVES FOR REMOVAL OF ORGANICS FROM A TWO-STAGE QUENCH

Condensate Water	Most Promising Alternatives	Possible Alternatives	Unlikely Alternatives
1st-Stage Quench	Incineration Evaporation Recycle to gasifier	Extraction with a low-boiling solvent	Stripping Adsorption Extraction with a high-boiling solvent
2nd-Stage Quench	Extraction with a high-boiling solvent	Adsorption Extraction with a low-boiling solvent	Stripping Evaporation Incineration

of the stream. The first stage quench would contain the most high-boiling solutes; therefore, the use of a low-boiling solvent for solvent extraction would be recommended. A high-boiling solvent would be more difficult to regenerate and may tend to build up heavy solutes over time. Depending on the size of the first stage quench stream, evaporation combined with incineration may be an attractive alternative for treatment. As discussed in Chapter I, the incineration scheme presented by Lienhard and Winkler (1983) can provide essentially a total treatment for the condensate water. Although incineration involves high energy costs, the completeness of treatment for this small stream in one step may be economically attractive over a multi-step process. Alternatively, direct injection of the 1st-stage quench into the gasifier may also be an attractive alternative. The presence of high-molecular-weight solutes in the first stage quench water would make adsorption and stripping unlikely alternatives for treatment.

Energy savings could be accomplished by using a high-boiling solvent for treatment of the second stage condensate water. The buildup of heavy solutes in the solvent should not be as much of a problem, since the heavy solutes should be concentrated into the first-stage quench water. Since the dihydroxybenzenes should not be present in the second stage quench water, simple distillation may be sufficient for regeneration of a high-boiling solvent, eliminating the need for back extraction of dihydroxybenzenes into base. Alternatively, the second stage quench water could be treated with a low-boiling solvent via the Phenosolvan or Chem-Pro processes; however, a higher solvent-to-water ratio would be required. Bulk adsorption of the organic solutes onto a polymeric resin such as Amberlite XAD-4 may be another alternative for treatment, since the higher-molecular-weight solutes suspected of fouling the resins would not be present. As discussed previously, stripping would not remove the hydroxybenzenes from water, due to the low relative volatility of these solute with respect to water.

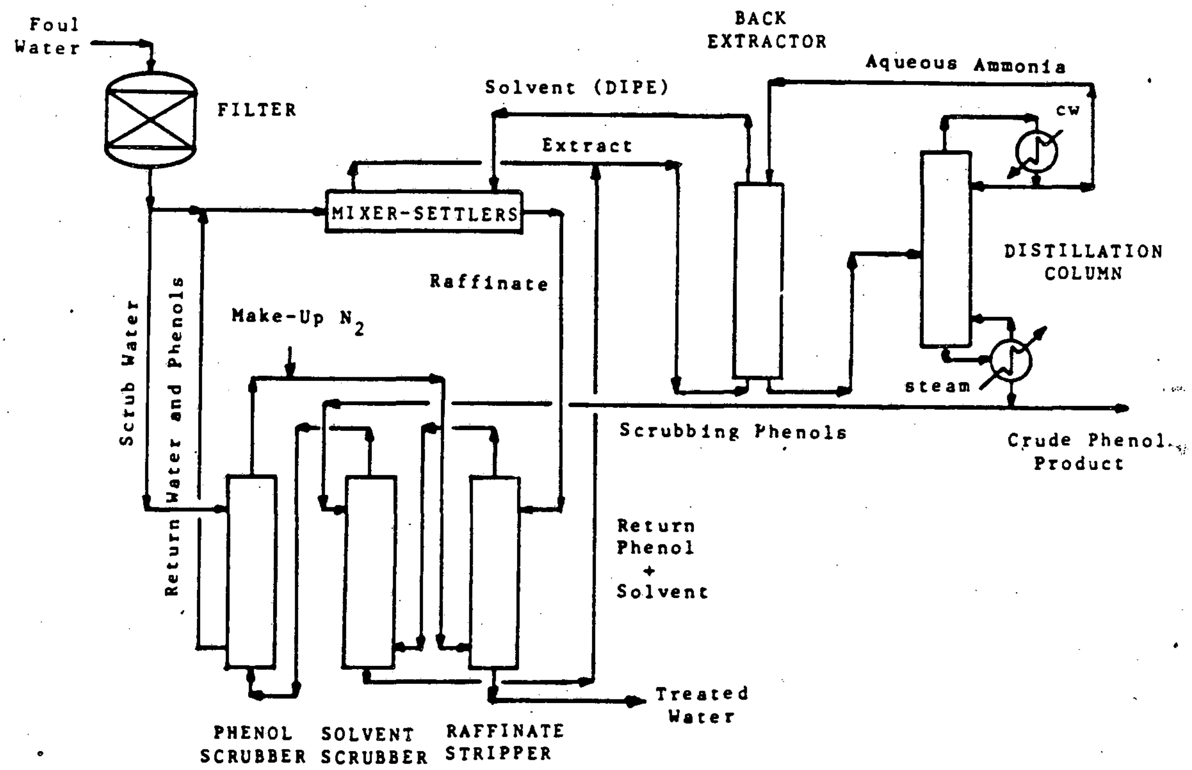
IV-E-2. Ammonia Recycle

The potential merits of using ammonia for solvent regeneration and regeneration of polymeric adsorbents has already been discussed above. In addition, the use of ammonia and carbon dioxide (i.e., aqueous ammonium bicarbonate) has been suggested as a possible means for regeneration of weak-base anion-exchange resins. Ammonia and carbon dioxide are inexpensive byproducts of the condensate water treatment, and their use should be exploited.

For the two-stage quench design discussed above, a low-boiling solvent such as DIPE can effectively remove the phenolic solutes from water, with distribution coefficients low enough to enable back extraction into aqueous base. Figure IV-6 illustrates the Phenosolvan process (Figure IV-1) modified to use ammonia regeneration of DIPE. Use of ammonia for regeneration could substantially reduce the steam consumption for regeneration since the amount of aqueous ammonia taken overhead in the distillation column would be much less than the DIPE taken overhead in the original design.

FIGURE IV-6

MODIFIED PHENOSOLVAN PROCESS USING AMMONIA FOR SOLVENT REGENERATION



IV-F. References

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CHAPTER V

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

V-A. Summary and Conclusions

The goal of this work has been to identify the major constituents in coal gasification condensate water and to assess treatment alternatives for these waters. Chapter I has presented what was known about these waters prior to this work and included an evaluation of process alternatives which have been suggested in the literature. In addition, the background for the source and need for treatment of the condensate waters was discussed. The review of the literature demonstrated that more characterization work was necessary to determine accurately the treatability of the condensate waters, and that several treatment alternatives required further investigation.

The characterization work in Chapter II was almost completely restricted to analysis of a condensate water sample obtained from Run-101 of the Lurgi slagging fixed-bed gasifier at the Morgantown Energy Technology Center (METC) in Morgantown, West Virginia. The analyses of the condensate water sample identified 95.8% of the chemical oxygen demand and 100% of the total organic carbon present. In addition, essentially 100% of both the organic nitrogen- and organic sulfur-containing compounds were also identified.

The major finding in this work was that thiocyanate was being measured in the chemical oxygen demand (COD), organic nitrogen, and organic sulfur measurements and that polysulfide was also measured in the COD and organic sulfur measurements. The organic sulfur balance assumed that polysulfides were present in the form of bisulfide ion (S_1S^{2-}) Additionally, low-molecular-weight solutes (acetonitrile, acetone, and methanol) were found to contribute greatly to the COD of a sample of Grand Forks Energy Technology Center (GFETC) condensate water. These compounds were not found to be present to as great an extent in the METC Run-101 condensate water. The difference in composition between the condensate waters was attributed to changes in coal feed and operating conditions of the gasifiers as well as quench circuit design. It was observed that lower grades of coal, such as lignite, produced waters with a greater organic content, and in particular more low-molecular-weight compounds. 5,5-Dimethyl hydantoin, which had been reported in other condensate waters, was found at much lower concentration in the METC condensate water.

The treatment experiments described in Chapter III yielded useful treatment data and identified several potentially attractive alternatives. Data collected on the extractability of condensate water solutes into methyl isobutyl ketone (MIBK) confirmed the superiority of MIBK over diisopropyl ether (DIPE) for extracting condensate water solutes. In addition, tributyl phosphate (TBP) was found to be a very strong extractant for the majority of the condensate water solutes. TBP was found to offer the advantage of lower regeneration costs compared to low-boiling solvents such as DIPE and MIBK. Use of the condensate water byproduct ammonia for regeneration of solvents was investigated and the criteria for its use were determined.

Adsorption experiments revealed that both activated carbon and a synthetic resin, Amberlite XAD-7 (Rohm and Haas), were effective for removal of catechol and 5,5-dimethyl hydantoin (5,5-DMH) from water.

These solutes were least extracted and identified as potential candidates for adsorption. Activated carbon was found to be more effective for removal of these solutes than was the synthetic resin; however, the phenolic compounds such as catechol were found to be unrecoverable from activated carbon by solvent regeneration. On the other hand, 5,5-DMH was found to be removable from activated carbon using methanol as a regenerant. Amberlite XAD-7 was found to be regenerable by methanol after adsorption of both catechol and 5,5-DMH.

Anion exchange was investigated as a means for recovery of thiocyanate from condensate water. Strong-base resins were found to be most effective; however, these resins demonstrated poor regeneration characteristics. Weak-base resins were also investigated and found to have better regeneration characteristics than the strong-base resins. The criteria for regeneration of weak-base resins was developed, and regeneration alternatives were discussed. Regeneration of a weak-base resin with ammonium bicarbonate solution was one topic that showed promise for future development.

Stripping organic solutes from condensate water was also assessed. Calculations based on rough estimation of activity coefficients demonstrated that quantitative removal of the majority of the condensate water solutes by stripping would be uneconomical.

Chapter IV discussed promising treatment alternatives for the condensate water. Current extraction processes, such as the Phenosolvan process, would not remove solutes such as thiocyanate and 5,5-DMH effectively from the condensate water. Adsorption appears to be the only method that can achieve removal of 5,5-DMH from the condensate water. Likewise, anion exchange is the only promising alternative for thiocyanate removal.

Also discussed in Chapter IV is the interfacing of inorganic and organic removal processes. The advantage of placing traditional stripping operations for dissolved gas removal after a solvent extraction process is to combine the solvent recovery step with the dissolved gas removal. This combination is useful only when a low-boiling solvent is used. Significant savings may be realized through the use of a high-boiling solvent and performing dissolved-gas removal as the first operation.

Chapter IV also demonstrates the advantage of using a two-stage quench circuit design instead of a single quench. A two-stage quench is expected to concentrate the majority of the salts and the dihydroxybenzenes into a relatively small stream, while the majority of the condensate water would be almost salt-free and contain only the hydroxybenzenes and lighter solutes. The relatively small volume of first-stage quench water would allow rigorous treatment by methods such as incineration. The treatment costs for the second-stage quench should be less. This opens options of using alternative treatment processes such as adsorption and extraction with a high-boiling solvent.

The concept of using recycled ammonia for regeneration of adsorbents and extractants was identified as a potential area for further development. In addition, the use of ammonium bicarbonate for regeneration of a weak-base anion exchange resin is of interest.

V-B. Recommendations

The characterization of condensate water is essentially complete and no further work is recommended in this area. However, further work is necessary for assessing new treatment alternatives for the condensate water and developing the concepts discussed in this work.

The impact of a two-stage quench circuit design on the gasification process and the distribution of solutes in the condensate water products must be assessed. Much of this information could be obtained through computer modeling using reliable estimations of activity coefficients.

The potential for using a high-boiling solvent such as TBP should be further investigated. Experiments need to be performed to determine the distribution coefficients of the dihydroxybenzenes in TBP-diluent mixtures in order to determine the optimal TBP concentration and the optimal diluent. Once the optimal TBP-diluent system has been identified, the aqueous solubility losses of TBP and the diluent must be assessed. Experiments using aqueous ammonia to remove dihydroxybenzenes from TBP need to be carried out to acertain the optimal aqueous concentration of ammonia and to assess the stability of TBP in the process.

Adsorption onto synthetic resins should be investigated for the treatment of the second-stage quench water. The quench water from a second stage of a two-stage process should not contain solutes that irreversibly adsorb, thereby allowing solvent regeneration. In addition, the use of ammonia for regeneration of adsorbents needs to be futher investigated.

Finally, more work needs to be performed on the use of weak-base anion-exchange resins for the removal of thiocyanate from condensate water, and the use of ammonium bicarbonate regeneration of anion-exchange resins.

APPENDIX A

THEORETICAL CHEMICAL OXYGEN DEMAND (COD) AND TOTAL ORGANIC CARBON (TOC) VALUES FOR CONDENSATE-WATER SOLUTES

Listed in Table A-1 are the values of the theoretical chemical oxygen demand (COD) and total organic carbon (TOC) of the condensate water solutes used in this work.

The theoretical COD values of the oxygenated hydrocarbons (e.g. phenolics) are based on the oxidation of the compounds to CO_2 and water. As discussed in Chapter II, the COD values of the nitrogen-containing compounds are based on conversion of the nitrogen atoms to ammonia. Also, the COD values of the sulfur-containing species are for the oxidation of the sulfur atoms to sulfate.

The TOC values reported in Table A-1 are simply the mass of carbon atoms per mole of solute, divided by the molecular weight of the solute.

TABLE A-1

THEORETICAL CHEMICAL OXYGEN DEMAND (COD) AND TOTAL ORGANIC CARBON (TOC) VALUES OF CONDENSATE-WATER SOLUTES

	Theoretical Values	
Compounds	mg COD/mg Compound	mg TOC/mg Compound
Hydroxybenzenes:		
Phenol	2.38	0.765
Cresol	2.52	0.777
Xylenol	2.62	0.786
o-Methoxy Phenol	2.06	0.677
Dihydroxybenzenes:		
Catechol	1.89	0.654
Resorcinol	1.89	0.654
Hydroquinone	1.89	0.654
4-Methyl Catechol	2.06	0.677
Naphthols	2.55	0.832
5,5-Dimethyl Hydantoin	1.12	0.468
Low-Molecular-Weight Organics:		
Acetone	2.20	0.620
Acetonitrile	1.56	0.283
Methanol	1.50	0.375
Thiocyanate	1.10	0.207
Polysulfide Sulfur (Assumimg S^0S^{2-})	3.50	0.0

APPENDIX B

GAS CHROMATOGRAPHIC ANALYSIS OF METC RUN-101 CONDENSATE WATER

The gas chromatographic analysis of the METC Run-101 condensate water was performed on both packed and capillary columns using a Model 3700 Gas Chromatograph (Varian Associates) equipped with a flame ionization detector (FID). A packed column GC analysis was used for the quantification of the low-molecular-weight solutes (acetone, acetonitrile, and methanol). Capillary GC analysis was used to obtain a separation of the condensate-water solutes for later GC-MS identification.

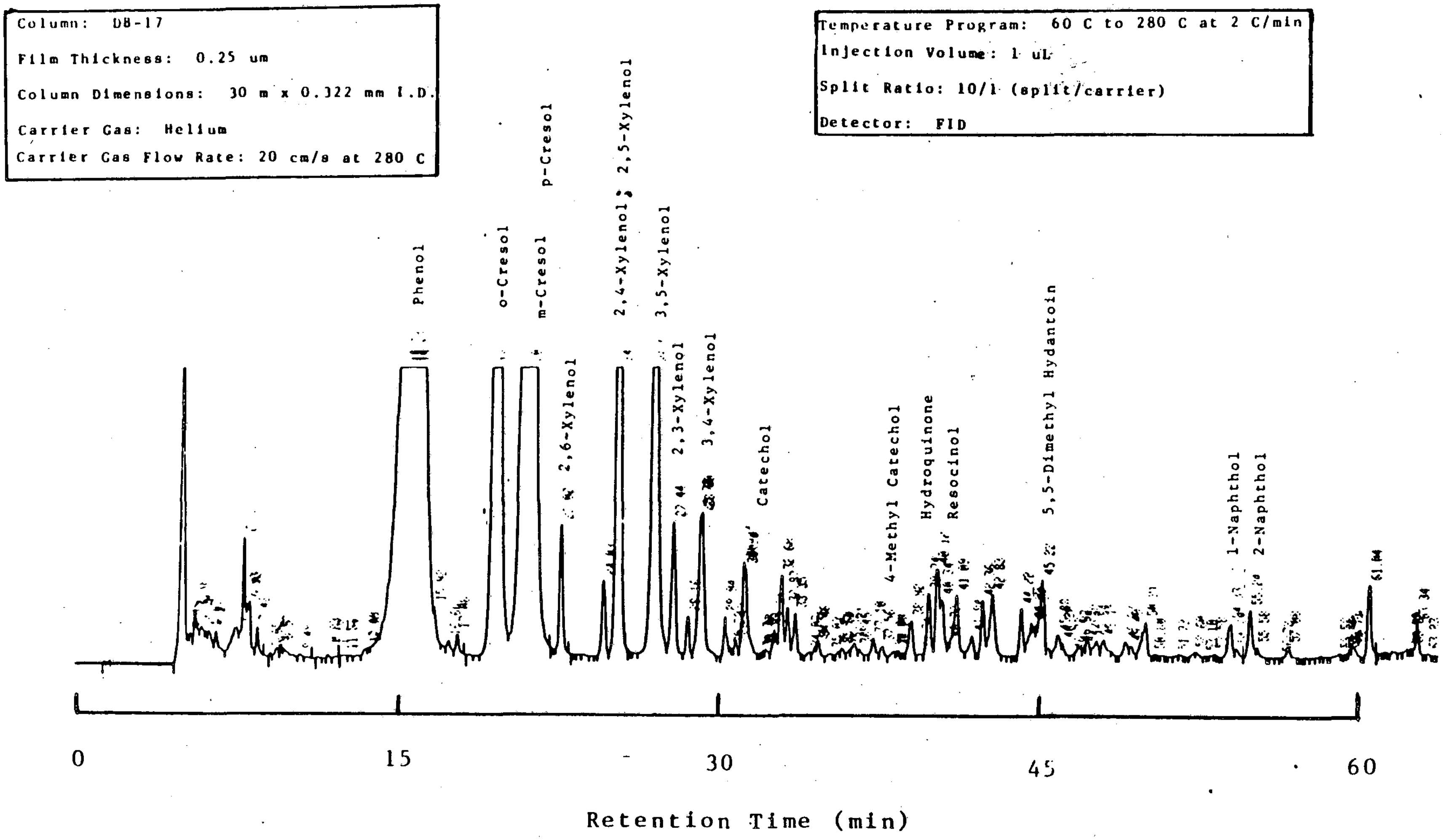
Presented in Figure B-1 is the chromatogram for the sample analysis performed on a DB-17 capillary column (J&W Scientific), along with the conditions used for the separation. The DB-17 column has a bonded methyl phenyl-polysiloxane phase and is of intermediate polarity.

Figure B-2 presents chromatogram and conditions for the separation of the condensate water sample on a DB-Wax capillary column (J&W Scientific). The DB-Wax column has a bonded polyethylene glycol phase and is highly polar. Use of the DB-wax column yielded well shaped peaks for the highly polar solutes (i.e., 5,5-dimethyl hydantoin and the dihydroxybenzenes) which were previously not attainable with the DB-17 column.

Illustrated in Figure B-3 is a summary of the packed GC analysis of the condensate water using a Porapak-Q (Waters Associates) column. The chromatogram in Figure B-3 demonstrates that only the low-molecular compounds are separated effectively under these conditions.

FIGURE B-1

SEPARATION OF METC RUN-101 CONDENSATE WATER SOLUTES ON A DB-17® CAPILLARY COLUMN FOR MS IDENTIFICATION

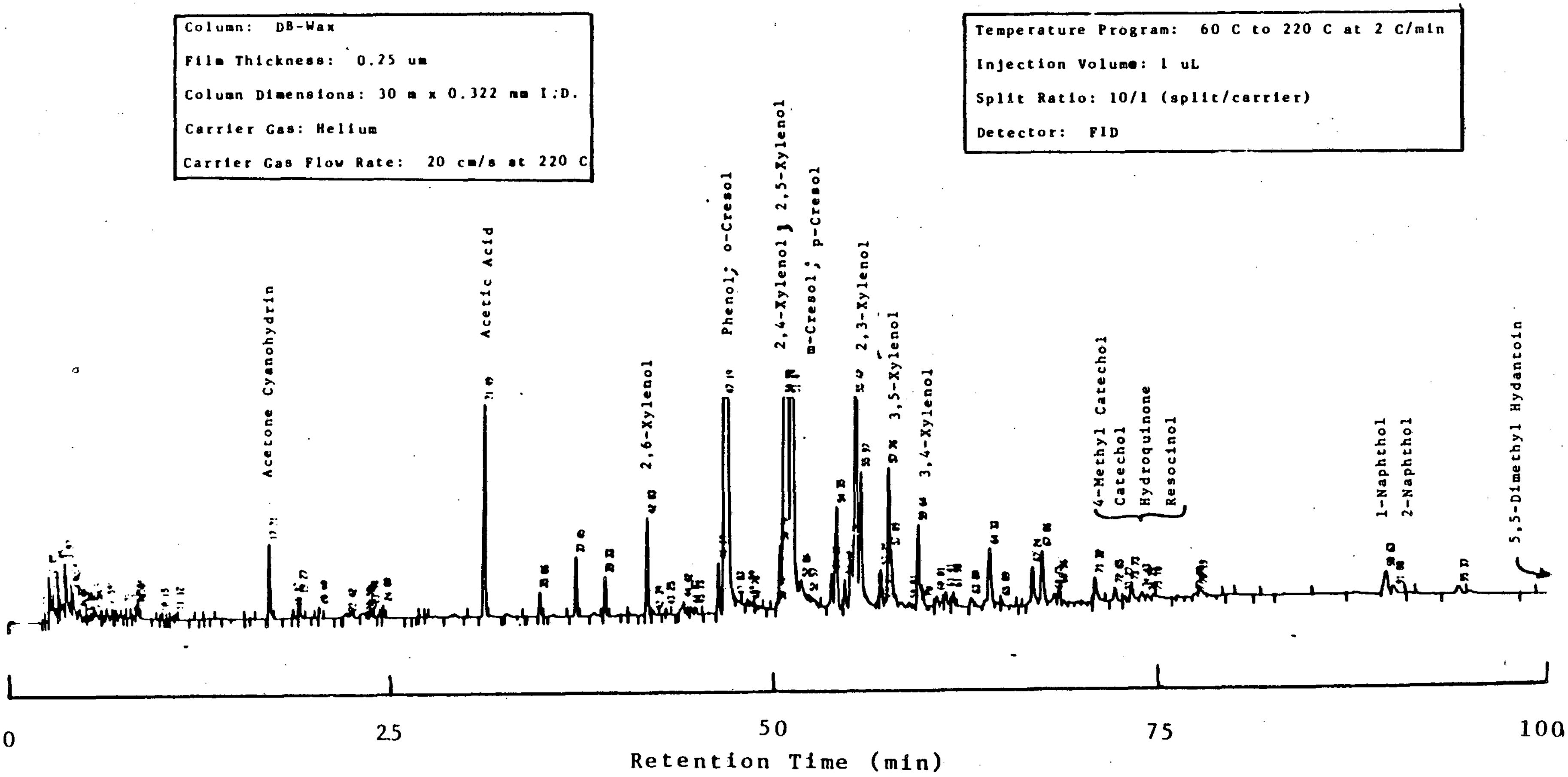


Column: DB-17
Film Thickness: 0.25 um
Column Dimensions: 30 m x 0.322 mm I.D.
Carrier Gas: Helium
Carrier Gas Flow Rate: 20 cm/s at 280 C

Temperature Program: 60 C to 280 C at 2 C/min
Injection Volume: 1 uL
Split Ratio: 10/1 (split/carrier)
Detector: FID

FIGURE B-2

SEPARATION OF METC RUN-101 CONDENSATE WATER SOLUTES ON A DB-WAX® CAPILLARY COLUMN FOR MS IDENTIFICATION

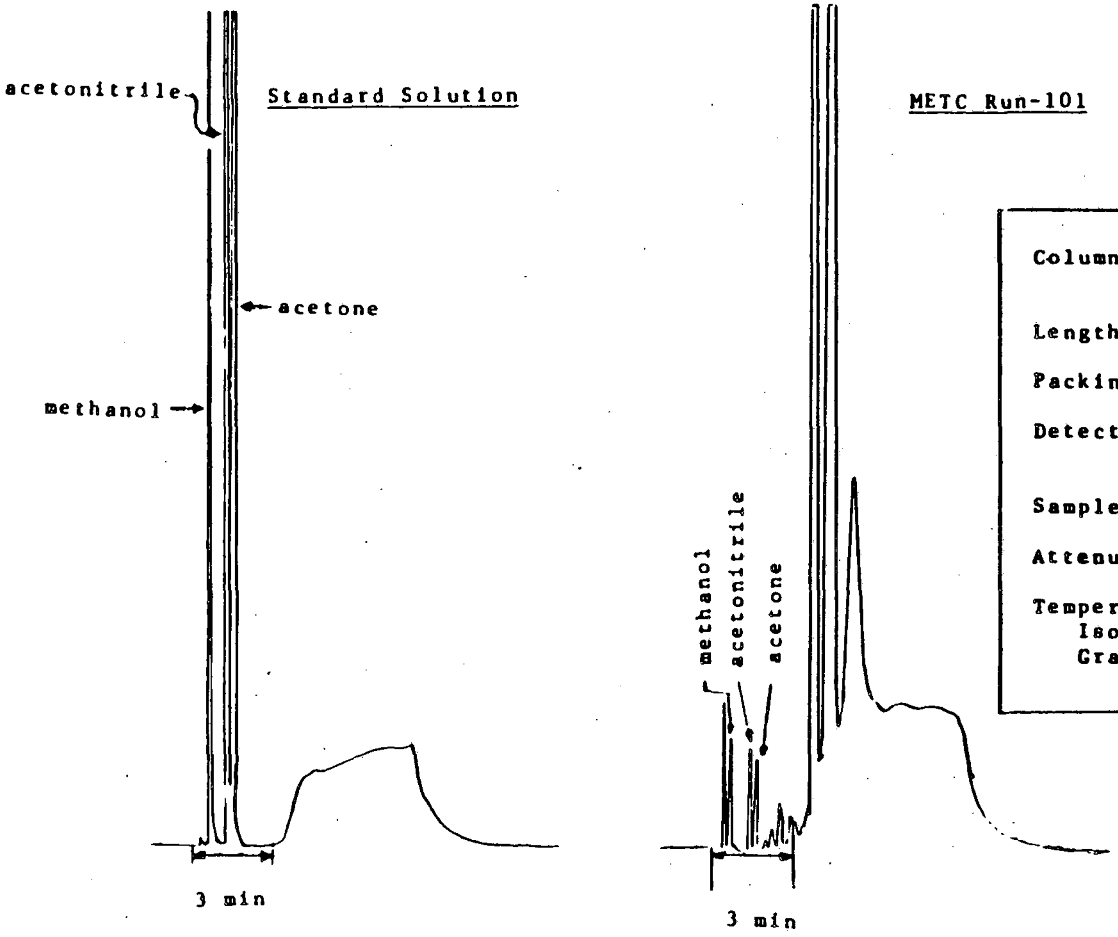


Column: DB-Wax
Film Thickness: 0.25 um
Column Dimensions: 30 m x 0.322 mm I.D.
Carrier Gas: Helium
Carrier Gas Flow Rate: 20 cm/s at 220 C

Temperature Program: 60 C to 220 C at 2 C/min
Injection Volume: 1 uL
Split Ratio: 10/1 (split/carrier)
Detector: FID

FIGURE B-3

SEPARATION OF LOW-MOLECULAR-WEIGHT SOLUTES IN METC RUN-101 CONDENSATE WATER ON A PORAPAK-Q® PACKED COLUMN FOR QUANTIFICATION



Column: 1/8 inch o.d. (26 gauge)
stainless steel

Length: 1 ft.

Packing: Porapak-Q

Detector: FID

Sample Size: 1μL

Attenuation: 32 x 10^{-11} amps/mV

Temperature Program:
Isothermal at 70 C up to 3 min
Gradient at 20 C/min at 3 min to 7 min

APPENDIX C

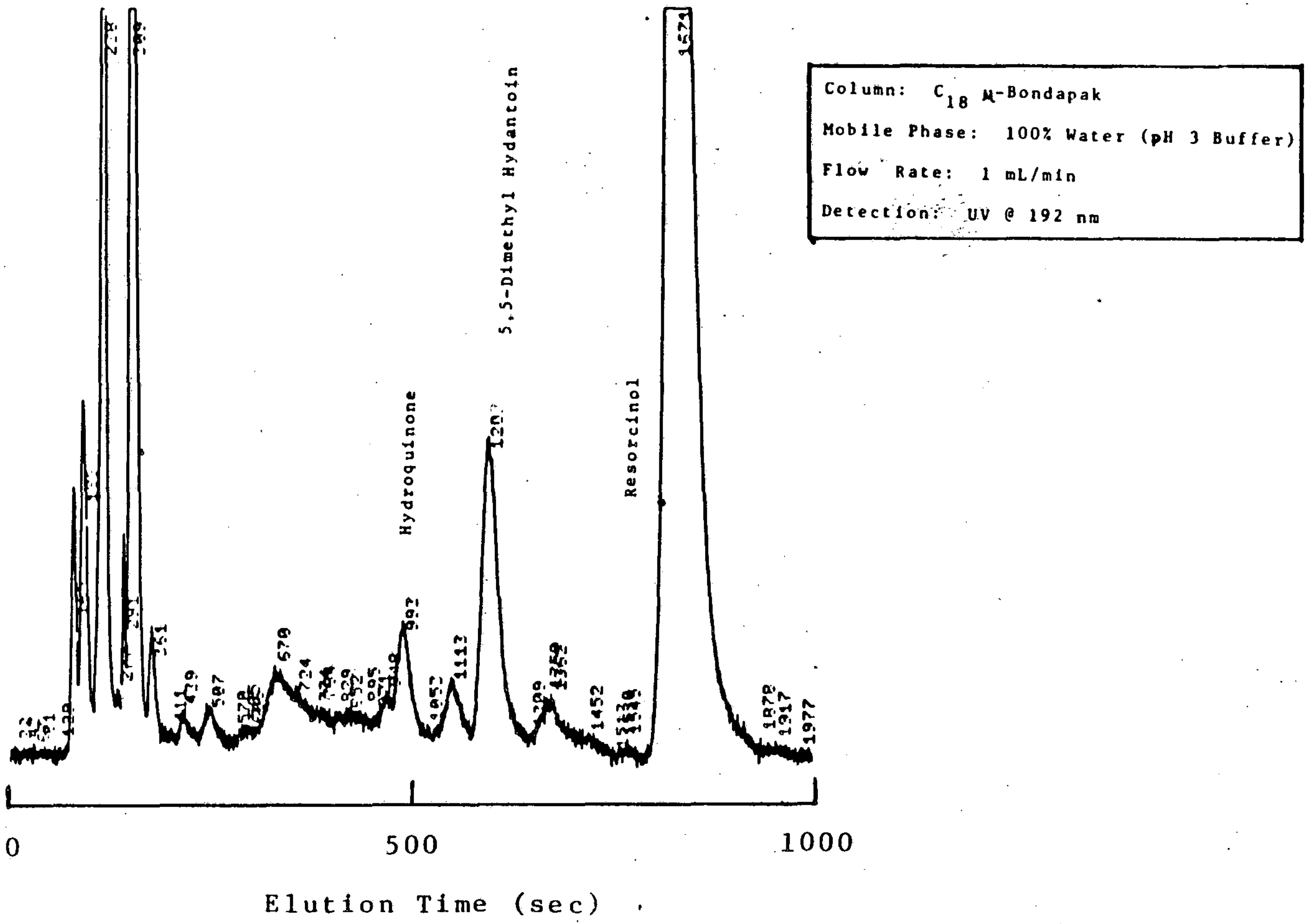
LIQUID CHROMATOGRAPHIC ANALYSIS OF METC RUN-101 CONDENSATE WATER

As described in Chapter II, both isocratic and gradient analyses were performed to quantify condensate water solutes. Separation was performed on a C_{18} μ-Bondapak column using a RCM-100 Radial Compression Module (both from Waters Associates). Detection of compounds was accomplished using a Model LC-75 Spectrophotometric Detector (Perkin Elmer).

The isocratic analysis yielded the concentrations of hydroquinone, resorcinol, and 5,5-dimethyl hydantoin. Gradient elution was performed to quantify the rest of the phenolic solutes. Detection of solutes was at 192 nm for the isocratic analysis and 280 mn for the gradient analysis. Both the isocratic and gradient analyses employed a pH-3 phosphate buffer to suppress ionization of the acidic solutes during separation. The preparation of the phosphate buffer is described in Section II-B-2b. Figure C-1 presents the chromatogram and summarizes the conditions used for the isocratic analysis. The chromatogram and conditions used for the gradient analysis are summarized in Figure C-2.

FIGURE C-1

ISOCRATIC HPLC ANALYSIS OF METC RUN-101 CONDENSATE WATER



Column: C_{18} μ-Bondapak

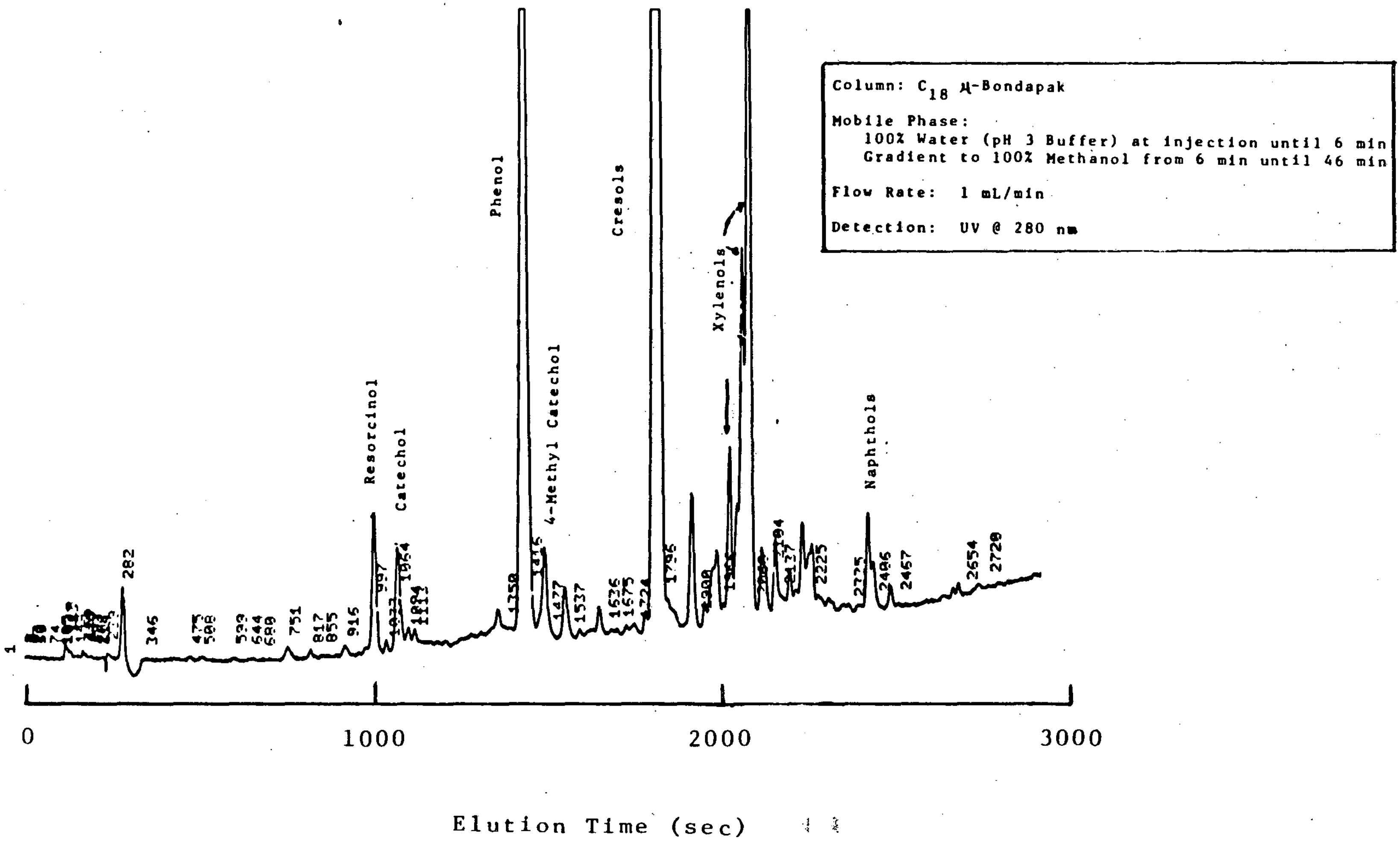
Mobile Phase: 100% Water (pH 3 Buffer)

Flow Rate: 1 mL/min

Detection: UV @ 192 nm

FIGURE C-2

GRADIENT HPLC ANALYSIS OF METC RUN-101 CONDENSATE WATER



APPENDIX D

PARAMETERS USED FOR THE SUPERRAK® FRACTION COLLECTOR

A Model 2211 Superrac Fraction Collector (LKB-Produkter AB) was used to collect HPLC fractions for MS analysis (Section II-B-1g). The fraction collector was interfaced with the Model LC-75 Spectophotometric Detector (Perkin Elmer) and operated in peak detection mode. The lag time between the detector and the sample collector head was determined by injecting an air bubble in to the HPLC system, with the column removed, and measuring the time which elapsed between the detector deflection and when the air bubble reached the fraction collector head. The parameters used for the fraction collection are summarized in Table D-1.

TABLE D-1

PARAMETERS USED FOR THE SUPPERRAK® FRACTION COLLECTOR

PROGRAM DESCRIPTION 2211 S U P E R R A C

LKB

Programme Memory 1 2 3 4 5

BASIC PARAMETERS

RAC [redacted] [redacted] C [redacted] [redacted]

MODE time [redacted] [redacted]

size 20:00 [redacted] min:s [redacted] [redacted]

FRACTION

number 84 tubes

ADDITIONAL PARAMETERS

WASTE size 20:00 [redacted] min:s [redacted] [redacted]

END time 60:00 h:min

DELAY size 00:58 min:s [redacted] [redacted]

CHROMATOGRAM WINDOW

NUMBER		1	2	3	4	5	6	7	8	9
TIME	start	0:00	:	:	:	:	:	:	:	:
	end	60:00	:	:	:	:	:	:	:	:

OPTIONAL PARAMETERS

PEAK code
1 threshold 2 0,1 mV
2 peak width 00:20 min:s
3 isocr. point 00:02 h:min
4 asymmetry 1.0

FUNCTION code
1 pumpscale 20
2 equilibrium 0.0 h:min
3 wait 0.0 h:min
4 fractionscale ① 60

APPENDIX E

MASS SPECTROMETRY ANALYSIS OF METC RUN-101 CONDENSATE WATER

Mass spectrometry (MS) yielded identification of several solutes in the METC Run-101 condensate water which were not identified in the GFETC condensate water samples analyzed by Mohr and King (1985) (See Reference in Chapter II). Using the techniques described in Chapter II, MS analysis successfully identified 1-naphthol, 2-naphthol, acetonitrile, and acetone cyanohydrin as condensate water solutes. In addition, MS analysis confirmed the presence of the phenolic solutes. Only the confirmation of newly identified solutes will be discussed here.

The presence of 1-naphthol and 2-naphthol was accomplished by GC-MS analysis employing a DB-17 (J&W Scientific) capillary column for the separation (See Chapter II and Appendix B) and operating the mass spectrometer in electron ionization (EI) mode for the identification. Presented in Figure E-1 and Figure E-2 are the MS outputs for 1-naphthol and 2-naphthol, respectively. Included in the figures are the eight largest mass-to-charge ratios (m/e) and their relative magnitudes for each pure solute, as reported by The Mass Spectrometry Data Centre (1983). The solutes were identified by the MS data system as the solutes providing the best fit to the data out of the 25,411 spectra cataloged in the MS library. The solutes provided a good fit to the data.

Acetic acid and acetone cyanohydrin were identified by GC-MS analysis using a DB-Wax (J&W Scientific) capillary column for the separation (See Chapter II and Appendix B) and operating the mass spectrometer in EI mode. Figure E-3 and E-4 present the MS outputs along with those reported for pure acetic acid and acetone cyanohydrin, respectively. As with the naphthols, these solutes were identified by the MS data system as providing the best fit to the data and demonstrated a good fit.

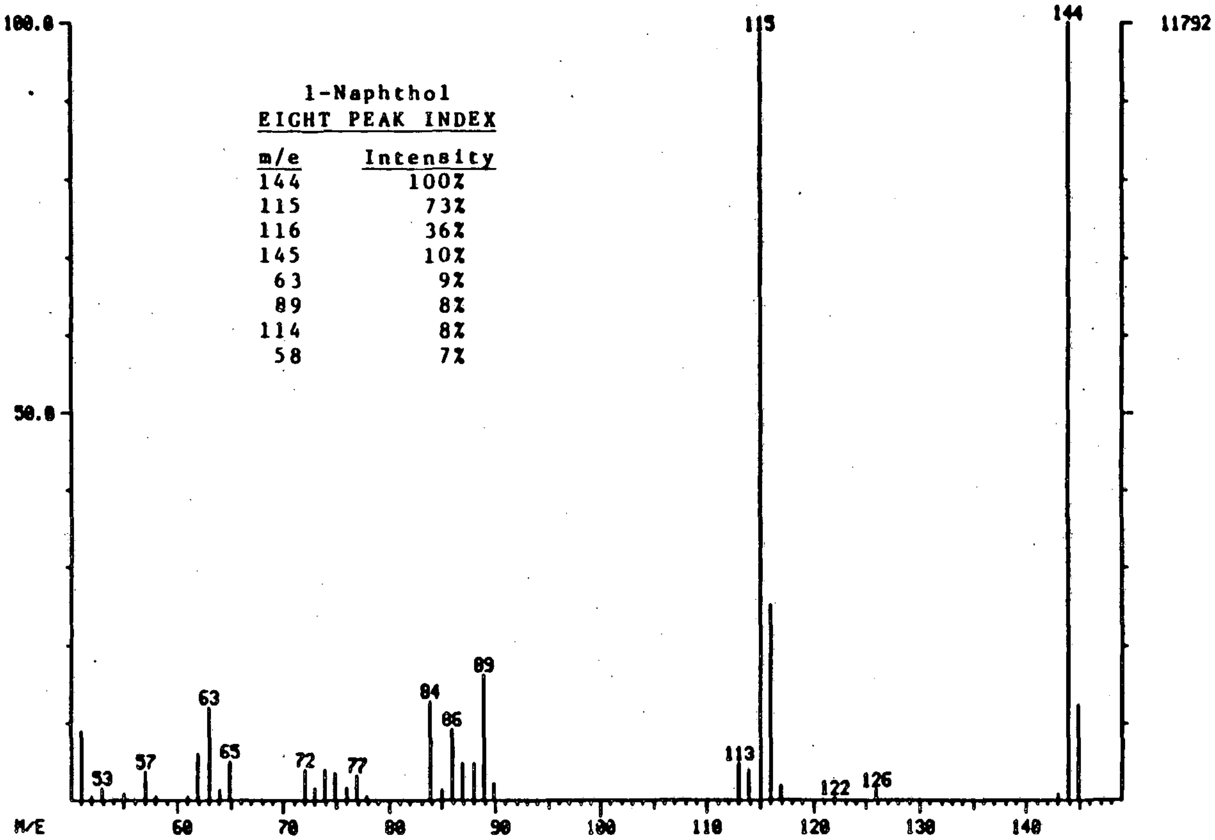
In addition to the compounds discussed above, thiocyanate in condensate water was also identified by MS analysis. Although the existence of thiocyanate in condensate waters was well documented before this work, it was not known that thiocyanate was responsible for unidentified peaks in the HPLC analysis. As described in Section II-B-1g, the HPLC was used to separate compounds to allow MS-probe analysis. Presented in Figure E-5 is the result of the probe analysis (chemical ionization (CI) mode) of a fraction that contained thiocyanate. The results in Figure E-5 demonstrate the unidentifed solute had a molecular weight of 59. Another sample of the same fraction was submitted for high resolution MS, the results of which are reported in Table E-1. The high resolution MS data revealed that thiocyanate (determined as HSCN) was the unidentifed solute, with a molecular weight of 59.

Reference

Mass Spectrometry Data Centre, Eight Peak Index of Mass Spectra, Vol 1, Part 1, 3rd Ed., The Royal Society of Chemistry, Nottingham, UK,1983.

FIGURE E-1

MS IDENTIFICATION OF 1-NAPHTHOL (EI MODE)

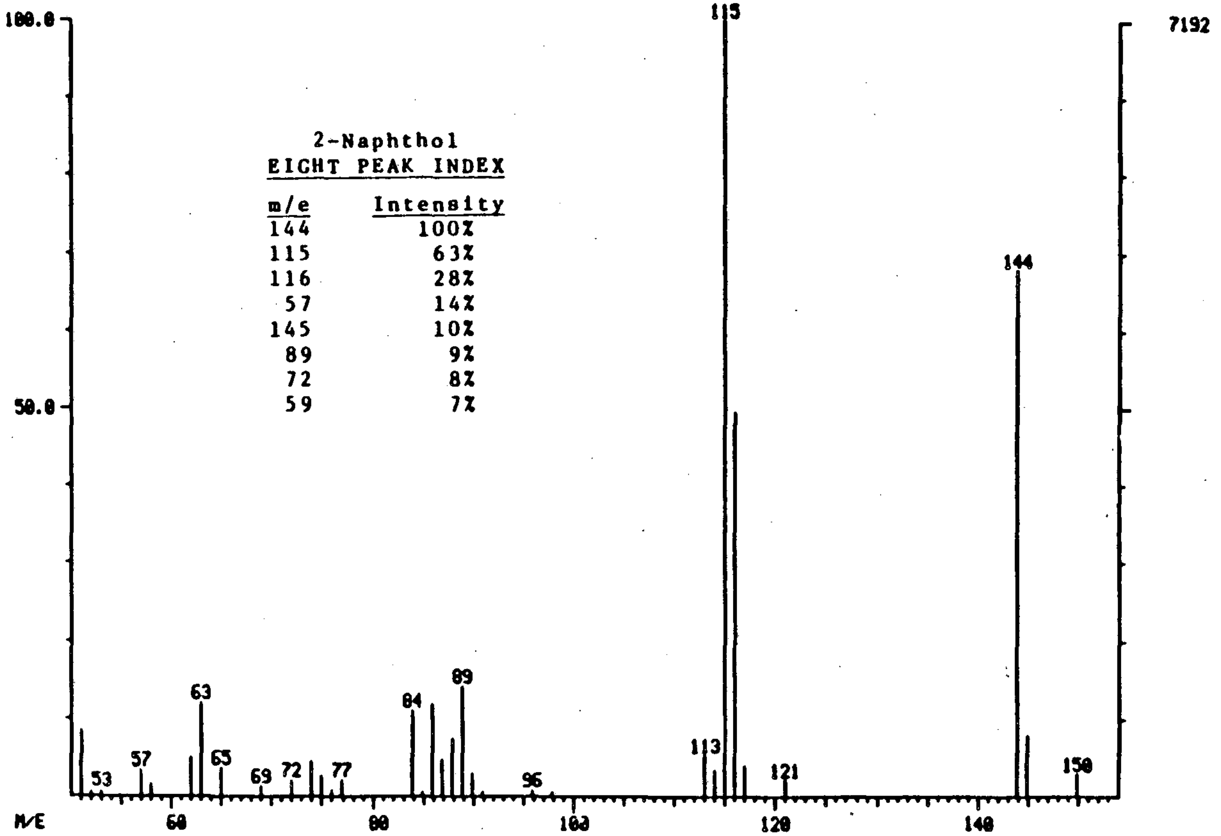


1-Naphthol
EIGHT PEAK INDEX

m/e	Intensity
144	100%
115	73%
116	36%
145	10%
63	9%
89	8%
114	8%
58	7%

FIGURE E-2

MS IDENTIFICATION OF 2-NAPHTHOL (EI MODE)

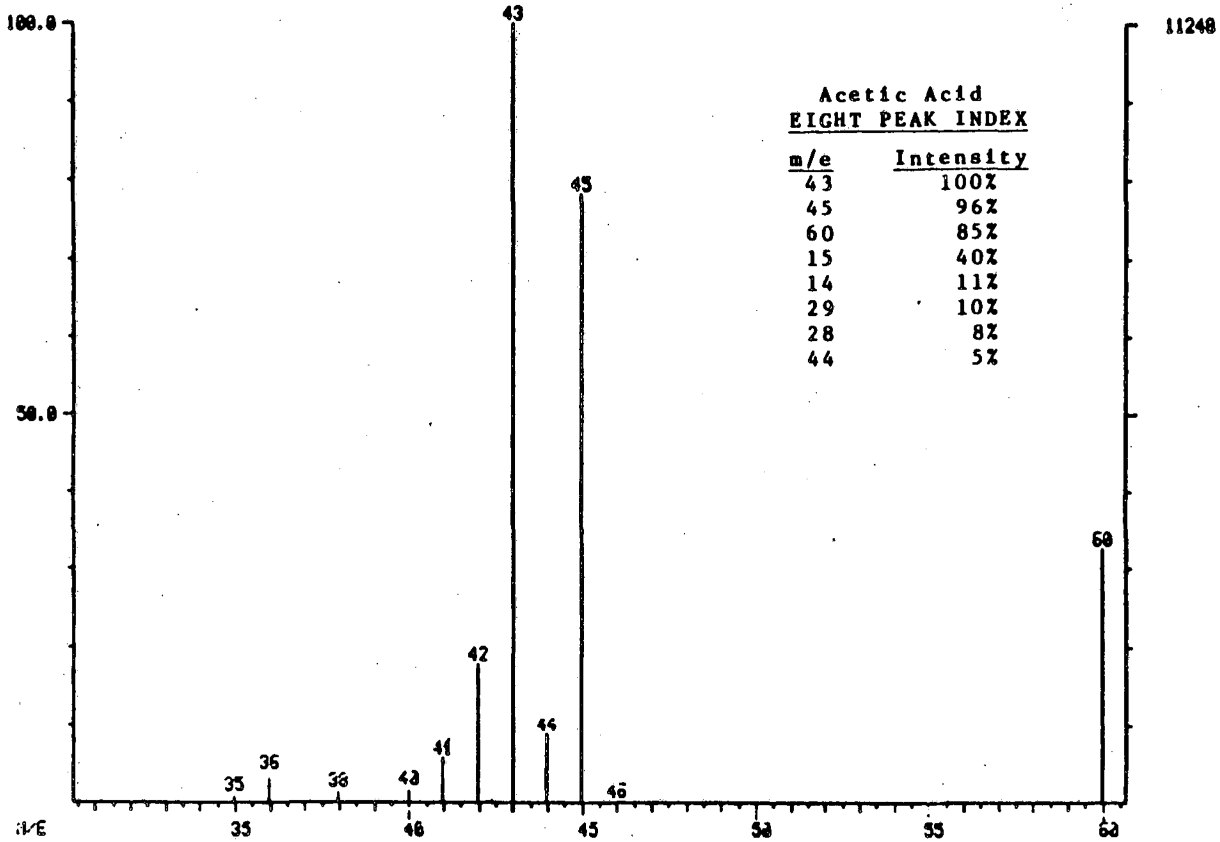


2-Naphthol
EIGHT PEAK INDEX

m/e	Intensity
144	100%
115	63%
116	28%
57	14%
145	10%
89	9%
72	8%
59	7%

FIGURE E-3

MS IDENTIFICATION OF ACETIC ACID (EI MODE)

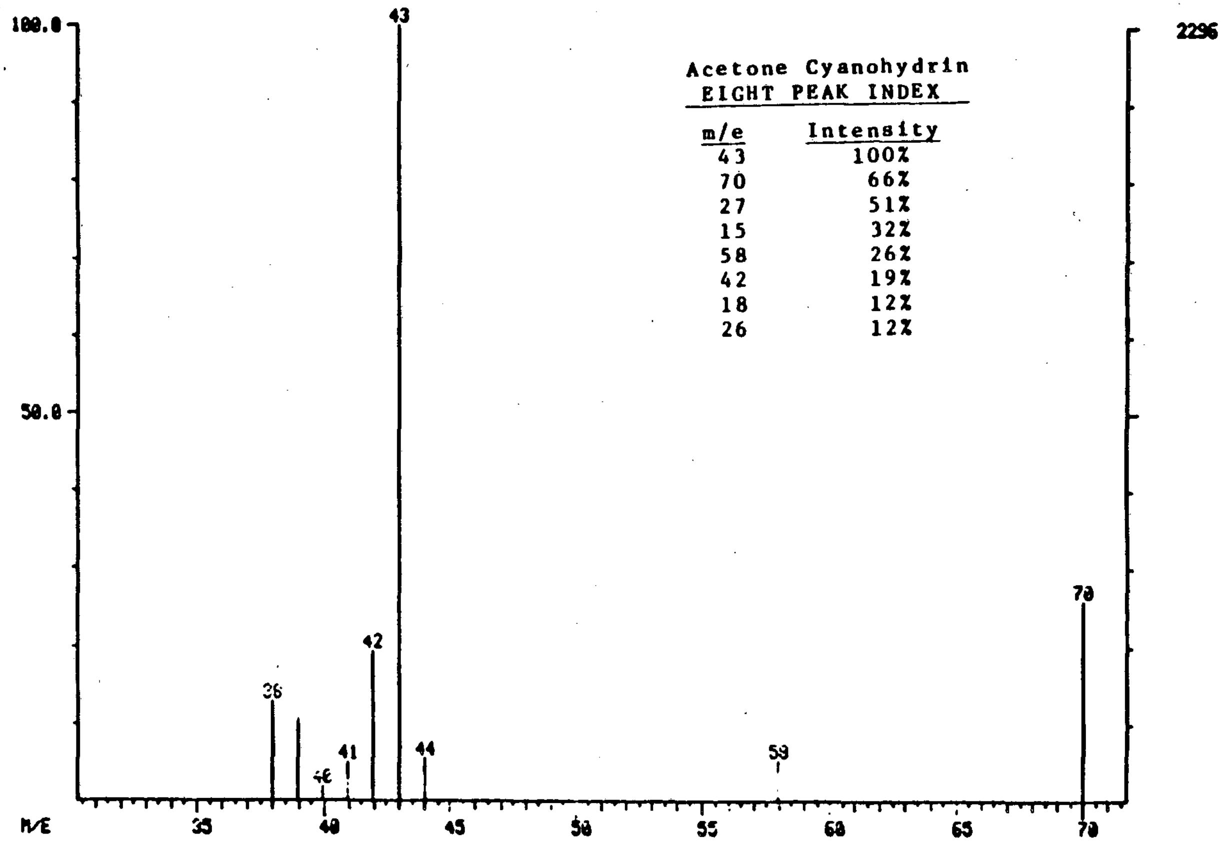


Acetic Acid
EIGHT PEAK INDEX

m/e	Intensity
43	100%
45	96%
60	85%
15	40%
14	11%
29	10%
28	8%
44	5%

FIGURE E-4

MS IDENTIFICATION OF ACETONE CYANOHYDRIN (EI MODE)



Acetone Cyanohydrin
EIGHT PEAK INDEX

m/e	Intensity
43	100%
70	66%
27	51%
15	32%
58	26%
42	19%
18	12%
26	12%

FIGURE E-5

MS IDENTIFICATION OF THIOCYANTE (CI MODE)

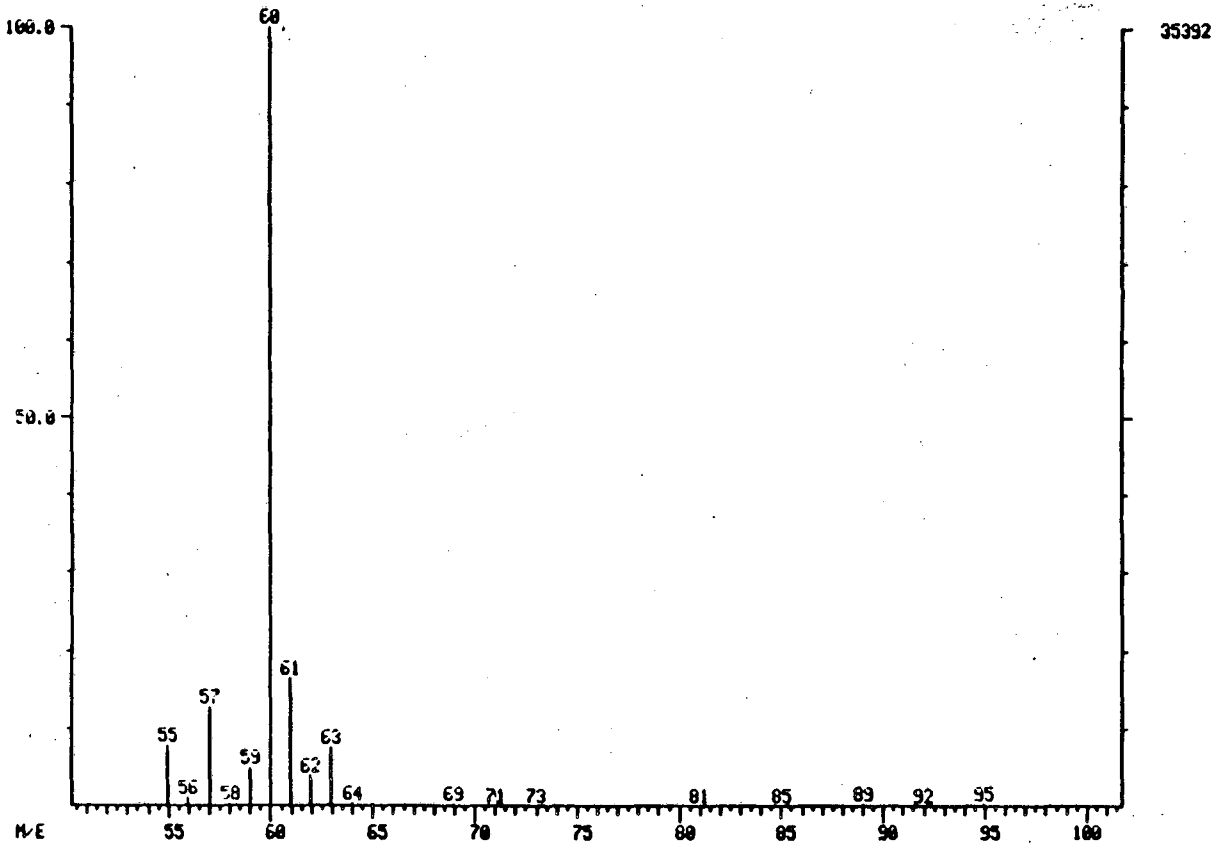


TABLE E-1

HIGH RESOLUTION MS DATA CONFIRMING THE PRESENCE OF THIOCYANATE

Elemental Composition							Mass (atomic units)		Deviation	Relative
C	C_{13}	H	N	O	^{32}S	^{34}S	Measured	Calculated	(MMU)	Intensity
*1	0	1	1	0	1	0	58.9825	58.9820	-0.5	100.00
*1	0	0	1	0	1	0	57.9746	57.9741	-0.5	11.19
4	0	9	0	0	0	0	57.0699	57.0694	-0.5	8.07
*1	0	1	1	0	0	1	60.9786	60.9785	-0.1	3.72
4	0	8	0	0	0	0	56.0620	56.0614	-0.6	3.63
1	0	0	0	0	3	0	59.9841	59.9834	-0.7	1.96
*0	1	1	1	0	1	0	59.9841	59.9818	-2.3	1.96
2	0	2	0	0	0	1	59.9841	59.9847	0.6	1.96
1	0	4	3	0	0	0	58.0414	58.0423	0.9	1.46
3	0	6	0	1	0	0	58.0414	58.0410	-0.4	1.46
0	0	2	3	1	0	0	60.0200	60.0202	0.2	1.43
2	0	4	0	2	0	0	60.0200	60.0189	-1.1	1.43
1	0	4	2	1	0	0	60.0310	60.0297	-1.3	1.13

---

* Confirms presence of thiocyanate.

(1) Analysis was limited to possible compounds containing carbon, nitrogen, oxygen, and sulfur.
(2) Calculated mass minus the measured mass.
(3) MMU = Millimass units (i.e., 10^{-3} atomic units).

APPENDIX F

SUMMARY OF EXTRACTION EXPERIMENTS

Presented in Table F-1 is a summary of the extraction experiments described in Chapter III. The solute concentration in the aqueous feed as well as that measured in the resulting raffinate are reported along with the solvent-to-feed ratio used in the extractions. Table F-1 also reports the equilibrium distribution coefficients, expressed as K_d, for each extraction, the average value of K_d, and the average deviations from the repeated trials. The value of K_d was based on the aqueous-phase analysis as described in Chapter III. The extractions were performed at 30 C. The table is organized in alphabetical order by solute name, and then alphabetically by solvent name.

TABLE F-1

SUMMARY OF EXTRACTION EXPERIMENTS PERFORMED

Solute	Solvent	Solvent/Feed (v/v)	Concentrations, (mg/L) Feed	Raffinate	K_d	Average K_d	Average Deviation
5,5-Dimethyl Hydantoin	Cyclohexanone	1.0	1000.	532.	0.93	0.92	3.6 %
			1000.	524.	0.96		
			1000.	548.	0.87		
	2-Methyl Cyclohexanone	1.0	1000.	765.	0.33	0.36	7.0 %
			1000.	740.	0.38		
	4-Methyl Cyclohexanone	1.0	1000.	663.	0.63	0.61	3.2 %
			1000.	648.	0.59		
	MIBK	1.0	1000.	830.	0.24		
	TBP	0.50	1000.	552.	2.20	2.2	1.5 %
			1000.	552.	2.21		
		0.75	1000.	448.	2.13		
m-Cresol	MIBK	0.30	1006.	17.5	235.	247.	3.3 %
		0.50	1006.	9.9	252.		
			1006.	9.8	255.		
p-Cresol	MIBK	0.30	987.	19.0	212.	229.	5.4 %
		0.50	987.	10.7	228.		
			987.	9.9	247.		

TABLE F-1 (Continued)

Solute	Solvent	Solvent/Feed (v/v)	Concentrations, (mg/L)		K_d	Average K_d	Average Deviation
			Feed	Raffinate			
Hydroquinone	Furan	1.0	1000.	979.	<0.02		
	4-Methyl Cyclohexanone	0.5	1000.	684.	26.1		
	MIBK	0.375	1000.	261.	9.44	9.6	1.2 %
		0.50	1000.	205.	9.68		
	TBP	0.50	1000.	12.3	164.	166.	0.7 %
			1000.	12.2	166.		
	50 wt% TBP in Dodecanol	0.50	1000.	67.7	30.5	30.2	1.2 %
			1000.	69.1	29.8		
	50 wt% TBP in Hexadecane	0.50	1000.	35.5	62.0	58.0	6.6 %
			1000.	40.3	54.4		
	50 wt% TBP in Phenyl Ether	0.50	1000.	42.7	43.6	43.8	0.5 %
			1000.	42.4	44.0		
Phenol	MIBK	0.50	988.	28.0	85.8	84.9	0.7 %
		1.00	988.	14.4	84.2		
			988.	14.4	84.6		
	TBP	0.50	988.	9.3	210.		
Resorcinol	33 wt% Benzophenone in IBHK	1.0	1000.	336.	2.3		

TABLE F-1 (Continued)

Solute	Solvent	Solvent/Feed (v/v)	Concentations, (mg/L)		K_d	Average K_d	Average Deviation
			Feed	Raffinate			
Resorcinol	33 wt% Benzophenone in Tributyrin	1.0	1000.	208.	3.8		
	4-Methyl Cyclohexanone	0.50	1000.	41.2	50.9	49.8	2.2 %
			1000.	42.9	48.7		
	MIBK	0.375	1000.	158.	17.8	18.0	0.8 %
		0.50	1000.	42.9	18.1		
	Tributyrin	1.0	1000.	153.	4.3		
2,3 Xylenol	MIBK	0.25	875.	7.4	582.	611.	3.2 %
		0.30	875.	5.9	610.		
			875.	5.7	640.		
2,4 Xylenol	MIBK	0.30	929.	8.8	440.	436.	0.9 %
			929.	8.9	432.		
2,6 Xylenol	MIBK	0.30	836.	6.0	574.	576.	0.6 %
		0.40	836.	4.5	578.		
			836.	4.4	584.		
3,5 Xylenol	MIBK	0.4	679.	3.5	814.		

MIBK = Methyl Isobutyl Ketone   IBHK = Isobutyl Heptyl Ketone   TBP = Tributyl Phosphate

APPENDIX G

PHYSICAL PROPERTIES OF VARIOUS SOLVENTS AND DILUENTS

Table G-1 presents the physical properties of various solvents and diluents examined in this work. The moelcular weight, melting point (C), boiling point (C), density (g/cm^3), and vapor pressure (torr) at 20 C are reported where information was available. The sources of the data are noted at the bottom of the table.

TABLE G-1

PHYSICAL PROPERTIES OF VARIOUS SOLVENTS AND DILUENTS*

Solvent/Diluents	Molecular Weight	Melting Point (C)	Boiling Point (C)	Water Solubility (mg/L)	Density at 20 C (g/cc)	Pressure at 20 C (torr)
Benzophenone	182.21	48.1	305.9	insoluble(2)	1.146	<0.1(1)
Cyclohexanone	98.15	-16.4	155.6	23,000(5)	0.9478	4.(2)
Dodecanol	186.32	26.	255.	insoluble(2)	0.8309	<0.1(2)
Furan	68.08	-85.6	31.4	10,000(4)	0.9514	---
Hexadecane	226.45	18.2	287.	insoluble	0.7733	<0.05(2)
Isobutyl Heptyl Ketone	184.32(1)	<-75.(1)	218.2(1)	<100(1)	0.8166(1)	<0.1(1)
2-Methyl Cyclohexanone	112.17	-13.9	165.	20,000 - 40,000	0.9250	---
4-Methyl Cyclohexanone	112.17	-40.6	170.	for mixture of isomers(4)	0.9138	---
Methyl Isobutyl Ketone	100.16	-84.7	116.8	17,000(5)	0.7978	5.(2)
Phenyl Ether	170.21	---	257.9	v. slightly soluble(2)	1.579	<0.1(2)
Tributyl Phosphate	266.38	---	289.		0.9727	0.003(3)
Tricresyl Phosphate	369.37	11.	410.	insoluble(2)	1.1955	---
Tributyrin	302.37	-75.	305.	---	1.0350	---

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* All data from Weast (1984), unless otherwise noted.
(1) Union Carbide Chemical and Plastics Div. (1981); (2) Perry and Green (1984); (3) Burger (1984)
(4) Flick (1985); (5) Riddick and Bunger (1970)

Table G-1 (Continued)

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APPENDIX H

ACTIVITY COEFFICIENTS AND VAPOR PRESSURES OF VARIOUS CONDENSATE WATER SOLUTES

This section presents the procedures used to obtain the infinite dilution activity coefficients and the vapor pressures reported in Table III-9 (Chapter III).

Vapor pressure data at 100 C for all the solutes, with exception of methanol, were calculated from equations and constants reported by Weast (1973). The methanol vapor pressure data were calculated from a relationship given by Weast (1984). The vapor pressure equations for the solutes were reported to be valid over a range of temperature that included 100 C, except those for methanol and acetonitrile which were reported valid up to 80 C. An estimate of the vapor pressure for these two solutes was obtained by extrapolation to 100 C.

The aqueous infinite dilution activity coefficients for acetone, methanol, acetonitrile, and phenol at 100 C were obtain from infinite dilution activity coefficients (γ_i^{inf}) reported by Gmehling et. al. (1981). The value of γ_i^{inf} for acetone was reported at 100 C; however, γ_i^{inf} for acetonitrile, methanol, and phenol were reported at 60 C, 25 C, and 44 C, respectively. The values of γ_i^{inf} at 100 C were obtained by assuming the systems formed regular solutions, and then using the fact that for regular solutions ln (γ_i) varies as 1/T (Reid et. al., 1977). The activity coefficients for catechol, resorcinol, and hydroquinone at 100 C were estimated in the same manner from the activitiy coefficients at 25 C reported by Greminger et. al. (1982).

Infinite dilution activity coefficients for the cresols were estimated from the aqueous solubility of these solutes in water by:

$$\gamma_{iw}^{inf} = 1/x_{iw}^{sat} \qquad \text{(Eq. H-1)}$$

where x_{iw}^{sat} is the mole fraction solubility of component i in water. Equation H-1 is identical to equation III-6 and subject to the same limitation, that is, a low mutual solubility of these solutes with water. The solubilities of the cresols in water at 25 C were obtained from Morrison and Boyd (1973) and were all near 0.4 mole %, allowing the use of Equation H-1. Again the solutes were assumed to form regular solutions with water in order to estimate the values of γ_i^{inf} at 100 C.

The activity coefficients for the xylenols were estimated from the extraction data for these solutes reported in Table III-1. Values of K_x were calculated from the K_d values reported for the extraction of the xylenols from water into methyl isobutyl ketone (MIBK) at 30 C. K_x is related to the activity coefficient of solute in water (γ_{iw}) and the activity coefficient of the solute in the solvent phase (γ_{is}) by:

$$K_x = \gamma_{iw}/\gamma_{is} \qquad \text{(Eq. H-2)}$$

Equation H-2 is identical to Equation III-5 in Chapter III. The activity coefficients of the xylenols in MIBK were assumed to be the same as the activity coefficients of the cresols in MIBK. Writing Equation H-2 for m-cresol and for the xylenol of interest, and dividing the two expressions leads to:

$$K_x(\text{m-cresol})/K_x(\text{xylenol}) = \gamma_{\text{cresol-w}}/\gamma_{\text{xylenol-w}} \quad \text{(Eq. H-3)}$$

The activity coefficients for the xylenols in water were then calculated from the activity coefficients obtained above for m-cresol in water, and the ratio of the distribution coefficients of these solutes into MIBK. The calculation yielded estimated activity coefficients at 30 C and regular solution theory was then used to estimate the activity coefficients at 100 C.

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