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A Membrane-Organic Phase Oxidation Process for the
Destruction of Toxic Organics in Hazardous Wastewaters

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ABSTRACT

The examination of the extraction/oxidation of organic solutes in a two phase oxidation process was undertaken to discern the important parameters and the process mechanism of this system. Several parameters were adjusted to measure their effect on the disappearance rate of each organic from the water phase. The water to PFD volume ratio proved to be the most sensitive parameter affecting the disappearance rate, although temperature was also significant. Comparison with one phase oxidation systems demonstrated that the water/PFD system improved on the reduction of organics from the water phase. B-naphthol oxidation increased over 50% in a 2/6 water/PFD volume ratio compared with the water phase oxidation. Phenol, which had the smallest distribution coefficient of the three organics tested, showed a significant reduction rate in the two phase system which was greater than a water phase oxidation system operating at higher pressures. Naphthalene and an H-coal wastewater also showed more oxidation in the two phase system than in a single water phase system. These results show that two-phase oxidation is a viable process and testing of the total membrane-oxidation system is in order. The feasibility of membrane concentration step is also demonstrated with model organics and actual wastewaters.

DESCRIPTORS: Hazardous Materials; Toxins; Oxidation; Wet Oxidation Process; Phenols; Pesticides; Herbicides; Membranes; Membrane Processes

IDENTIFIERS: Liquid Phase Oxidation; Toxic Organics

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CHAPTER I. INTRODUCTION

The overall objective of this project is to determine the possibility of treating wastewater containing such hazardous components as phenolics, PAH compounds, pesticides, and synfuel plant effluents by a two-step process. This process consists of concentration (for dilute wastes) of the waste stream using commercially available membranes followed by a novel organic-phase oxidation step. For concentrated wastes the membrane step is not required. Experimental work for this project is focused on the latter step since no previous data are available. Studies were concentrated on the model compounds B-naphthol, phenol, and naphthalene, although an actual H-coal waste stream was also evaluated.

The single phase oxidation scheme, Wet Air Oxidation (WAO) or Zimmerman Process, has received a lot of attention as a viable means of treating highly concentrated organic wastewaters. The high temperatures and pressures of this system provide good reaction conditions for combustion of the organics, however, this system has experienced several drawbacks in its development. The biggest problem is the need to employ additional treatment to the effluent due to the incomplete combustion of the organic constituents. These intermediate compounds are possibly formed due to the lack of stoichiometric quantities of oxygen in the liquid phase. They resist further oxidation and must be treated in an additional system before the stream can be discharged or reused.

The oxidation of phenol and naphthalene in a WAO process were conducted by Harris et al (11) at ORNL - Oak Ridge National Laboratory. They found that the organics exhibited three stages of oxidation; an induction period, fast oxidation and slow oxidation. The reaction had a first order dependence on the organic concentration. They reported higher activation energies of 22.3 kcal/mole for phenol and 29.9 kcal/mole for naphthalene. They also investigated the oxidation of these components in the biological sludge of a coal conversion pilot plant. The results indicated significant mass transfer limitations due to sludge particles which lowered the oxidation rates.

Numerous reaction intermediates were identified in this study. For phenol, they found significant concentrations of hydroquinone and catechol

in the first five minutes of oxidation, and over longer periods, succinic acid and glycolic acid were observed. The oxidation of naphthalene produced very little TOC reduction (small amount of CO₂ formed). Phthalic acid anhydride and possibly naphthoquinone were the intermediates formed from naphthalene oxidation.

Pruden and Ferguson (18) investigated the oxidation of phenol by WAO. They found an activation energy of 10.8 kcal/mole. Mass transfer of oxygen was determined to be the rate limiting step at large phenol concentrations (>200 mg/l). This small value of the activation energy may be attributed to the mass transfer limitations.

Pruden and Le (19) employed phenol and nitrilotriacetic acid in their investigation of the WAO process. They reported that the volatile phenol may be partially oxidized in the gas phase with the presence of liquid water as a catalyst. This conclusion was proposed due to the similar activation energies of liquid and gas phase reactions, as well as the relative mass transfer rate of oxygen into the liquid as compared with the mass transfer rate of phenol into the vapor. They also verified other works that the reaction was first order in phenol and oxygen.

Baillod, Faith and Masi (1) investigated the Wet Air Oxidation of phenol to determine the formation of intermediates and to track their time profiles. They found a significant discrepancy of reduction rates between the phenol concentration and the TOC. The vapor phase oxidation was determined to be unimportant under their reaction conditions. The products of reaction included formic acid, acetic acid, maleic acid, oxalic acid, succinic acid, acetone and acetaldehyde. Time profiles of these intermediates are shown in Figure 1. Formic and acetic acids are the major end products, while maleic and oxalic acids formed in the early stages, then drop off rapidly.

The Wet Air Oxidation of low molecular weight organic acids (propionic acid and butyric acid) was investigated by Williams et al (29). They reported a high activation energy of 32 kcal/mole for propionic acid. This indicated a high resistance of the lower carboxylic acids in WAO. The reaction mechanism was proposed to be a free radical mechanism with both propionic acid and butyric acid forming acetic acid and formic acids.

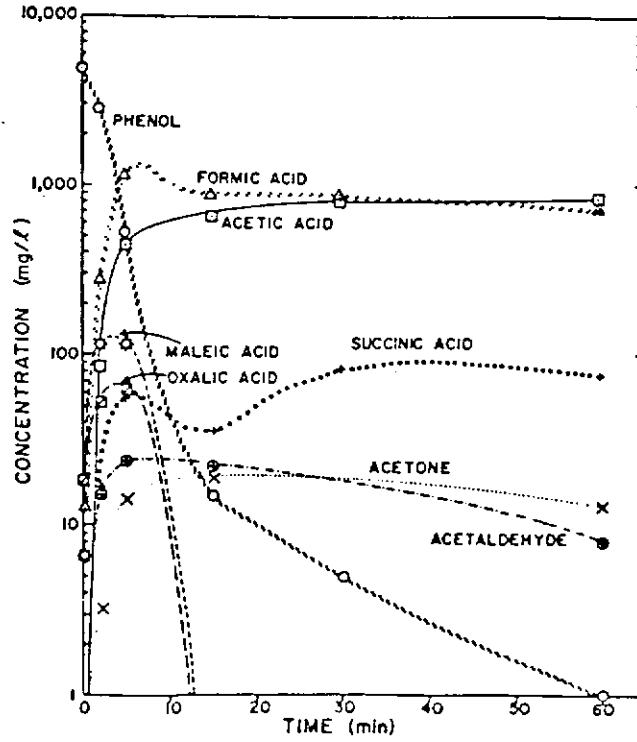


Figure 1 The formation of intermediates for the one phase oxidation of phenol (i)

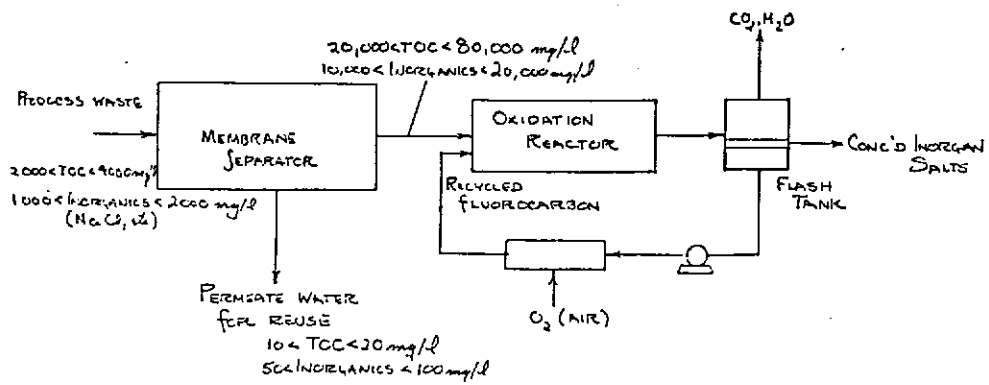


Figure 2 Proposed Membrane-Organic-Phase Oxidation Reactor System

Skaates et al (25) investigated the WAO of flucoese and found three distinct stages of oxidation - induction, rapid oxidation, and slow oxidation. The activation energy of the rapid oxidation stage was determined to be 22.4 kcal/mole which is considerably higher than those reported by other investigators.

A number of researchers have shown that oxidation at less severe conditions can be realized if catalysts are added to the system. Yunis (30) employed hydrogen peroxide and an iron catalyst system in a flucoese solution and found the oxidation proceeded to the same degree of conversion at lower temperatures and pressures than in the unmodified process, however, this system was only effective in a pH range of 2-4. Westman (27) investigated several oxidation schemes using hydrogen peroxide and a chromium(VI) catalyst system. He found that rapid oxidation occurred at a temperature of 170°C and a pressure of 750 psi, and the pH values were observed in the range of 7.0.

One of the most important applications of WAO has been in the treatment of sewage sludge from biological treatment units. Harding and Griffin (10) reported about the operation of a WAO operation located in Westchester County, New York. The original design called for a 90% reduction of organics from 5,000 GPD of sewage sludge with a 5% loading, however, after construction, the organic loading increased to 6.5%. Despite the increased loading, the WAO unit continued to operate with a 90% reduction in organic matter. This demonstrates the flexibility that a WAO unit can perform under a variety of conditions.

Wilhelmi and Ely (28) have proposed several alternative schemes that incorporate the WAO process with a biological treatment system and activated carbon particles. The carbon particles enable high concentrations of toxic organics to be treated without exposing the bacteria to toxic amounts. The combined sludge and carbon stream is an ideal feed stream for a WAO process. Tests by Burant (4) have shown that spent carbon can be completely regenerated by a WAO process.

Another important application of the WAO process has been in the pulp and paper industry. Teletzke (26) investigated the WAO process application for the chemical recovery of sulfite liquor. Spent sulfite liquors which contain high organic concentrations are oxidized by this process,

while the resulting liquor can be reused in the pulping process. The heat of oxidation together with the product gases can also be employed to generate mechanical energy and produce an energy surplus.

Indeed, several investigators have concluded that the WAO process can generate enough energy to maintain self sufficiency. Chou and Verhoff (6) estimated that an incoming waste stream with at least 8,000 mg/l of COD can generate enough energy to keep the system self sustaining. Above a COD of 40,000 mg/l nearly maximum efficiency of conversion to electricity was obtained.

An important area today is in the treatment of hazardous wastes generated by the organic chemical industry. Luciano (14) investigated its use for the disposal of polymers, which represent a significant waste disposal problem. The WAO process has been applied to the wastewaters generated by the coal conversion industries. Tests on H-coal washwater by Bhattacharyya (3) have resulted in significant reductions in the organic loading of the water.

The application of the WAO process is continuing to grow into new areas. Together with the two phase modification scheme, the WAO process could become a preferred wastewater treatment process.

Randall and Knopp (21), and Randall (20) have reported bench-scale wet air oxidations for many pure compounds. The compounds represented various categories from the EPA priority pollutant list. Destruction of 99+% was reported for acrolein, carbon tetrachloride, chloroform, cyanide, Malathion, pentachlorophenol (with catalyst), phenol pyrene, and several other compounds. Of reported materials kepone (31% destruction), Aroclor 1254 (63%), and 1,2-dichlorobenzene (69%) were the most refractory.

All the coal liquefaction processes as well as Eastern oil shale retorting processes produce high strength (up to 40,000 mg/l COD) organic and salts containing water which requires extensive treatment for water reuse and organic disposal. Some of the alternate processes proposed include reverse osmosis (17), biological process (15), autoxidation with air (16), non-catalytic, wet oxidation (31), and photochemical oxidation (9). Chou and Verhoff (6) have studied a process for power generation from wet air oxidation by using high COD (78,000 mg/l) wastes

from coal gasification wastes. Bhattacharyya and Karastelev (under an International Research Exchange Board Grant) recently studied the oxidation kinetics of aqueous phase (wet air oxidation) oxidation of phenolics, catechol, etc. at 150-250°C (300-1200 psi). These results will be compared with the proposed organic phase oxidation studies. Recent studies have focused on catalytic, wet oxidation of model compounds such as phenols (21,23), formic acid (2,8), and acetic acid (13).

Because of the low solubility of oxygen in water (10.9×10^{-7} mol/cm³ at 25°C and 1 atm) complete oxidation requires continual addition of oxygen to a one phase system. A trickle-bed oxidation reactor consisting of catalyst particles (CuO-ZnO) with cocurrent downward flow of air and water containing formic acid was studied as a model reactor system (8). The major transport effect that retarded the rate of oxidation and reaction was the gas-liquid mass transfer resistance. To overcome this retardation of rate it is proposed to use an organic medium in which the solubility and diffusivity of oxygen are higher than in water. At 37°C perfluorodecalin (boiling point = 142°C) dissolves 40 ml of oxygen/100 ml (7) compared to 2.4 ml/100 ml for water (22). These latter authors also present a diffusivity of oxygen in a fluoroamine twice the value of that for oxygen in water. No value for perfluorodecalin has been found, but it is also believed to be significantly higher than water.

The proposed two stage process is shown in Figure 2. The process water is concentrated first in the membrane separation by a factor of 10 to 20. In this way the volume of the reactor can be reduced significantly and the permeate water (low in salts and organics) can be reused directly. The oxygen-containing fluorocarbon is passed through the reactor with the concentrated solids stream (probably over a catalyst) and then to a phase separator where the CO₂ and H₂O are flashed off and the concentrated aqueous inorganics are withdrawn. Oxygen is resupplied to the fluorocarbon and it is recirculated to the reactor. This process is analogous to the Exxon Donor Solvent (EDS) process for coal liquefaction where the solvent is a recirculating hydrogen carrier. One big difference is that the EDS process requires a catalyst to add hydrogen to the solvent but the oxidation process does not since oxygen is carried physically (solubility) rather than chemically. Another important aspect of the

organic phase oxidation is that inorganics will prefer the aqueous phase and thus HCl corrosion problem will be minimized. It should be noted that perfluorocarbon liquids are stable to at least 400°C (24) and thus degradation is not expected.

CHAPTER II. RESEARCH PROCEDURE

A. Two-Phase Oxidation/Extraction Experiments

The experiments performed in this study were designed to obtain information about the system mechanisms. Equilibrium data was established for several organic solutes between water and PFD to gain an understanding of the extraction mechanism alone. One phase oxidation experiments were conducted to measure the oxidation potential of each phase. The methods used to obtain this information are described in this section. Table 1 is a summary of the various experimental parameters studied.

1. Sample Preparation

The organic solutions were prepared by measuring out the required amount of solid solute on a Mettler gram balance and dissolving it in double-distilled water to obtain one liter of solution. Equal molar solutions of B-naphthol and phenol were made. The B-naphthol solution of 500 mg/l was used because of its low solubility in water. The phenol solution was set at 326 mg/l. The copper acetate solution was made in a similar manner as described above and its concentration was set at 100 mg/l.

The maximum concentration of the naphthalene solution was established to be 42 mg/l at an elevated temperature. This proved unusable due to the small concentrations remaining in the water phase after each run. Therefore, the naphthalene was dissolved directly into the PFD. The maximum concentration was set at 175 mg/l which corresponds to a 100% stoichiometric oxygen concentration. Reagent grade (99+) chemicals were always used in our studies.

2. Extraction Runs

The organic solutions were contacted with equal volumes of the corresponding phase at room temperature ($21 \pm 2^\circ\text{C}$) in an 11 ml stainless steel bomb. The bomb was sealed tight and was shaken at 200 rpm for a period of 24 hours. Twenty four hours was required to insure that the system had reached equilibrium. Previous investigators (5) had shown

that naphthalene and B-naphthol required 24 hours to achieve equilibrium at room temperature.

After the required time had elapsed, the samples were removed from the bomb and placed in a centrifuge. The centrifuge separated the two phases more distinctly. The top layer (water) was then suctioned off using a 5 ml pipette until only a very thin film remained near the interface. It was placed in a test tube and was ready for analysis. The bottom layer (PFD) was also suctioned off employing another 5 ml pipette. A thin film of PFD was left near the phase boundary while the rest of the PFD was placed in a test tube and put aside for later use. The interface films were discarded.

3. Oxidation Runs

Pure oxygen was bubbled through the desired quantity of PFD using a gas diffuser. The transfer of oxygen to the PFD is very rapid, therefore a period of 10 minutes was sufficient to saturate the PFD. The organic solution was placed in an 11 ml stainless steel bomb at the desired ratio for each run. The oxygenated PFD was then immediately placed in the bomb and the bomb was sealed tight. The bomb was then clamped to the shaft of a variable speed motor. The shaft was lowered into a Tecam fluidized sand bath which had been set at the desired temperature for the oxidation run. The bomb was shaken at 200 rpm for all runs.

Time profiles were made for different parameter configurations. Time zero for all the runs was set at the beginning of the shaking process. Upon reaching the desired run time, the shaft was pulled out of the sand bath and immediately placed in a bucket of 7°C tap water which had a continuous stream of water flowing into it. The bomb remained in the water bath until it approached room temperature, this took about 5-10 minutes.

The sample was removed from the bomb and placed in a centrifuge for about 2-3 minutes. The water layer was then suctioned off the top, leaving a thin film near the interface. It was placed into a clean test tube and was ready for analysis. The PFD layer was also suctioned off and combined with other used PFD for later use. The residual film was discarded. The suctioning employed two clean 5 ml pipettes with a Fisher-Brand safety pipette filler.

4. Catalyst Runs

An equilibrium distribution of copper acetate between water and PFD was established. The copper acetate was distributed to the PFD phase with a starting concentration of 32 mg/l of Cu^{+2} in the water phase. At equilibrium, 13.5 ml/l of Cu^{+2} was present in the PFD.

The PFD containing Cu^{+2} was separated from the copper acetate water solution by the usual technique. This PFD was used for the catalytic oxidation runs. The catalytic oxidation runs were performed the same way as described above in the oxidation run section. Thus in all catalytic runs, the copper was present only in the PFD phase at the start of the run. Measurement of copper in the water phase was made after the run was completed.

5. The Reuse of Perfluorodecalin

Used PFD from previous experiments was oxygenated by bubbling oxygen through the liquid using a gas diffuser. This PFD was then placed in a bomb, the bomb clamped to the shaft, and lowered into the sand bath operating at 250°C. The bomb was shaken at 200 rpm for about an hour.

After completion, the bomb was quenched, the PFD was removed and placed into a clean test tube. A similar run with this PFD showed no difference between the used and fresh source of PFD. In oxidation runs, the reused PFD gave identical results for the same set of conditions.

6. Analytical Technique

The water samples were analyzed using a Varian Model 500 - High Performance Liquid Chromatograph. Prior to injection, the samples were filtered with a Millipore 0.45 micron filter. The HPLC column was a Varian Micropak MCH-10 which contains a stationary phase of 10 mm-silica with a monomeric layer of octyldecylsilane. The model phase was operated on a gradient 10/90 acetonitrile/water to a 90/10 acetonitrile/water in 40 minutes. The ultraviolet detector was operated at 220 nm waveland for most runs, a few were made at 254 nm and 280 nm wavelength. A typical set of run conditions and a chromatograph are shown in Fig. 3 80/ml of biphenyl was used as a reference peak for all HPLC runs.

TABLE 1
SUMMARY OF EXPERIMENTAL PARAMETERS AND RANGES

EXPERIMENT TYPE	TEMPERATURE (°C)	CONTACT TIME (MIN)	pH RANGE	TESTED SOLUTES	WATER/PFD RATIO
Extraction	21	24 Hours	-	Copper Acetate Naphthol Phenol Naphthalene	4/4
pH effects	21	24 Hours	1-12	Naphthol Phenol	4/4
Oxidation	150-250	0-100	1-11	Naphthol Phenol Naphthalene	8/0, 4/4, 3/5 2/6, 1/7, 0/8
Initial pH	200	0-60	1-11	Naphthol Phenol	3/5, 2/6
Water to PFD Ratio	150-250	0-90	6-9	Naphthol Phenol Naphthalene	8/0, 4/4, 3/5 2/6, 1/7, 0/8
Temperature Effects	150-250	0-70	9	Naphthol Phenol	3/5, 2/6
Use of Catalyst	200	1-10	9	Copper Acetate Naphthol Phenol	2/6
Contacting Time Prior to Oxidation	200	24 Hours	6-9	Naphthol	2/6
Effect of Starting Phase on Organic Concentration	200	0-50	9	Naphthol Naphthalene	4/4, 0/8

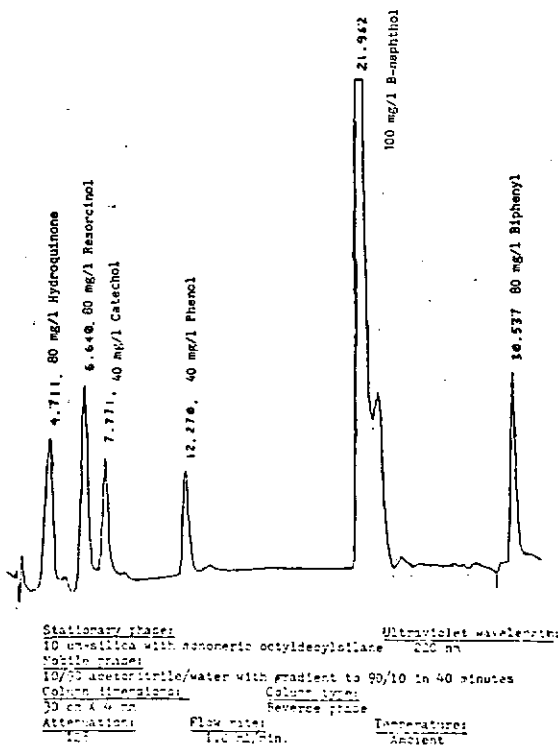


Figure 1 A typical HPLC chromatograph using the standard method

The water samples were also analyzed for TOC using a Beckman Model 915 Total Organic Carbon Analyzer. The samples were diluted to within the range of 10-40 ppm carbon. Residual carbon dioxide was purged from the system by lowering the pH and bubbling nitrogen through the sample. The pH was adjusted up to a range of 4-9 and then injected into the analyzer. The catalytic runs were analyzed for copper using a Varian Model AA-575 Atomic Absorption Spectrophotometer.

B. Membrane Experiments

Low pressure composite membranes (UOP and Film Tec) were used in all studies. Membrane studies were conducted in a batch (2000 cm³ capacity) and a continuous (spiral wound module) unit. Semi-batch operating mode provided concentration factors of 5X to 10X. Both model compounds (phenol, naphthol, resorcinol, naphthalene, organic acids) and actual wastes (H-coal synfuel wastewater and pesticide + metal containing waste) were investigated. Membrane operating processes ranged between 13 and 21 atmospheres.

CHAPTER III. DATA AND RESULTS

The destruction of organic solutes by the extraction/oxidation process in a two phase Wet Air Oxidation process is a complicated series of mass transfer and reaction steps. The high temperature and pressure of the system provide an ideal medium for high molecular bombardment and rapid changes in molecular configurations. With the added dimension of two immiscible phases and transfer between them, the true deterministic model of this system is a formidable problem to formulate. The measurement of diffusion coefficients, kinetic constants and equilibrium distribution coefficients are required to discern this model.

The experiments, performed in this study, were preliminary investigations into this complex system. These investigations have examined several important parameters that affect the extent of extraction/oxidation. The parameters adjusted in this study include the initial pH of the water phase, the water to PFD ratio, the temperature (pressure) of oxidation, the use of a copper catalyst, the shaking speed and the types of waste examined. The extent of extraction/oxidation varies greatly with the values of these parameters. In this section, this inquiry will examine the effect of these variables on the system and attempt to explain and understand these phenomena.

A. Results of Extraction Studies

The organic solute distributes between the water and the PFD phases due to an unequal chemical potential between the two phases. Equilibrium is achieved when the chemical potential is equal in both phases. The rate at which equilibrium is reached is dependent on the diffusion coefficient of the solute, the interfacial surface area between the two phases and the hydrodynamics of the system. Earlier investigations have shown that B-naphthol and naphthalene require twenty-four hours to reach equilibrium at room temperature (5). Preliminary results in this study found that equilibrium at 200°C was achieved close to twenty minutes. The extraction studies were conducted at room temperature and required twenty-four hours.

1. Measurement of Distribution Coefficients

Three organic solutes and one copper catalyst were examined in the water-PFD system. Equilibrium was attained and the measurement of the distribution coefficient for each solute was determined. Phenol, B-naphthol and naphthalene showed increasing distribution coefficients of 0.040, 0.103 and 94.0 respectively. The distribution coefficient for copper acetate was found to be 0.75 for this system. The order of the three organic solutes correspond to a decrease in their solubility in water.

The distribution behavior of these organic solutes is explained on the basis of their dipole moment, hydrogen bonding and their solubility in water. Phenol is highly soluble in water up to a concentration of 82,000 mg/l at room temperature (12). The phenol molecule has a polar configuration and readily forms hydrogen bonds with the polar water molecules. Thus phenol favors the water phase as opposed to the nonpolar PFD phase.

B-naphthol is only partially miscible in water yielding a maximum concentration of 740 mg/l at room temperature and elevated pH (12). The larger B-naphthol molecule is less polar than the smaller phenol molecule. It forms hydrogen bonds with the polar water molecules, however, the solvating properties of water are less effective on the larger molecule than for phenol. The distribution indicates that B-naphthol favors the water phase yet significant amounts transfer into the nonpolar PFD phase.

Naphthalene is almost insoluble in water having a maximum solubility of 30 mg/l at room temperature (12). The naphthalene molecule is nonpolar, it does not form hydrogen bonds with the polar water molecules. Little hydration of the molecule is observed. Naphthalene shows a high affinity for the nonpolar PFD phase and readily leaves the water phase.

The solubility parameters of these solutes are also important variables in determining the distribution of the solute between the two phases. The difference between the solute and solvent solubility parameters is affected in a similar manner by the criteria described above. The values of solubility parameters are determined from physical properties of the compounds. The solubility parameter is broken up into a polar and a nonpolar component. From the regular solution theory, the prediction of the distribution coefficient can be made from a knowledge of these polar and nonpolar components for each of the compounds in the system. The value of the interactive energy term in Equation 5 was determined by fitting the activity coefficient of the solute at infinite dilution in the PFD phase, to the experimentally determined values of the three organic solutes.

Table 2 shows the experimental and the predicted distribution coefficients for phenol, naphthol, naphthalene and copper acetate, as well as, the predicted values for other organic solutes. The predicted values demonstrate a reasonably good correlation with the experiments in this study. The order of extractability is well defined according to the physical properties of the systems. Although the predicted values are not accurate enough to be used in design work, they do give a clear indication of the extraction potential and can be used as a screening method. Naphthalene was predicted to have the highest distribution coefficient of the compounds considered and from experimental work, it does have the highest one of those tested.

The predictions were based on the solubility parameters, infinite dilution activity coefficients and the molal volumes of each component. In a similar manner, the solubility of the solute in water and the dipole moment are also indicators of the distribution coefficients. The dihydroxybenzenes are expected to have low distribution coefficients due to their high solubility in water and the polar nature of the molecules.

TABLE 2

EXPERIMENTAL AND PREDICTED DISTRIBUTION COEFFICIENTS*

SOLUTE	DISTRIBUTION COEFFICIENT**		REFRACTIVE INDEX	DIPOLE MOMENT	MOLAL VOLUME V_2 (Cm ³ /mole)	SOLUBILITY PARAMETERS	
	EXPERIMENTAL	PREDICTED				POLAR	NONPOLAR
Aniline	-	0.094	1.5863	1.6	91.2	3.364	10.31
Catechol	-	0.01	1.604	1.4	95.8	5.114	10.559
m-cresol	-	0.036	1.5438	1.8	104.6	5.416	9.689
p-cresol	-	0.030	1.5312	1.6	106.3	5.679	9.501
Hydroquinone	-	0.01	1.608	1.4	82.9	10.30	10.616
Naphthalene	94.0	161.5	1.4003	0.0	125.0	4.147	7.447
B-naphthol	0.103	0.169	1.6224	2.2	112.9	1.802	10.817
Phenol	0.040	0.018	1.5400	1.6	89.0	5.829	9.644
Pyridine	-	0.112	1.5095	2.3	80.6	5.317	9.174
3,5-Xylenol	-	0.214	1.512	1.8	108.6	1.628	9.213
Resorcinol	-	0.01	1.614	1.4	86.7	8.236	10.70
Copper Acetate (as Cu ⁺²)	0.75						

* TEMPERATURE - 21°C

** $K_D = C_A^{PF} / C_A^W$

Hydroquinone, which has the highest distribution coefficient of the three, is less polar than both catechol and resorcinol and has the lowest solubility in water of the three. All other organic compounds in Table 2 have predicted distribution coefficients that lie between phenol and B-naphthol. 3,5-xyleneol has a value close to B-naphthol and would be expected to show similar oxidation results as B-naphthol in the two phase system.

2. The pH Effect on the Distribution Coefficients

The distributions of B-naphthol and phenol between water and PFD were determined for various initial pH values in the water phase. Figure 4 shows the variation of the distribution coefficient of B-naphthol over the range of pH 1.0 to 12.0. The partition coefficient increases at the low and high side of the pH range and approaches a minimum value of 0.018 at a pH of 5.6. The distribution coefficients for phenol also show a similar trend as depicted in Figure 5. However, the variation of the distribution coefficient is less for phenol than for B-naphthol. The minimum value for phenol is 0.038 which occurs at a pH of 6.0. The distribution coefficient increases as the pH approaches the low and high side of the pH range.

The effect of pH on the distribution coefficient is linked to the solvation characteristics of water. Since both B-naphthol and phenol are polar molecules, they form hydrogen bonds with the water molecules. The water molecules surround the organic molecule because of the strong polar interaction. However, at low pH, the abundance of hydrogen ions causes the water molecules to congregate near these ions. Because the cations are more strongly hydrated than the neutral organic molecules, the organic compounds become less hydrated and thus, they are more freely available to move into the PFD phase.

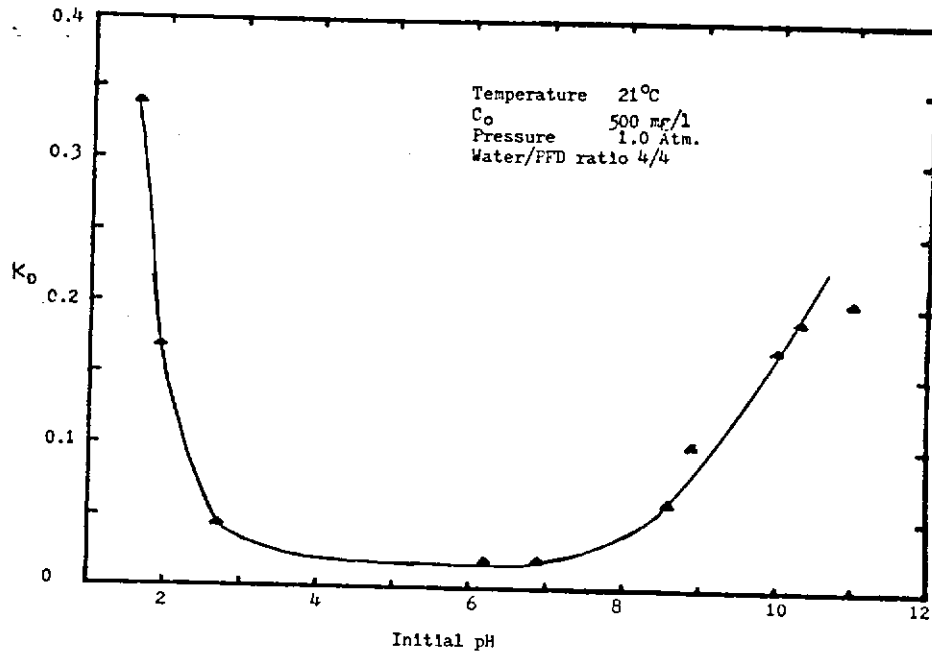


Figure 4 The effect of pH on the distribution coefficient of B-naphthol

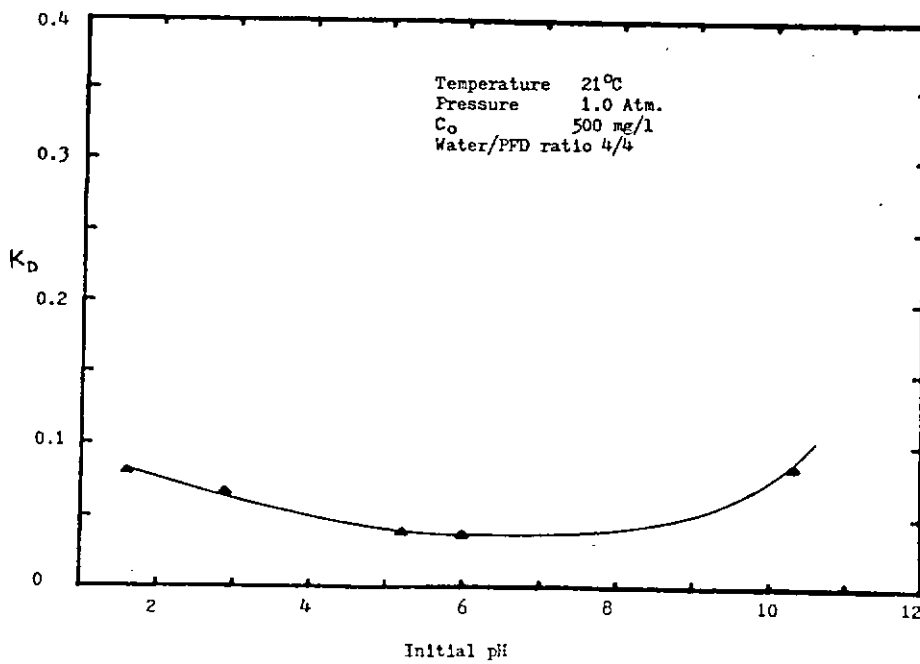


Figure 5 The effect of pH on the distribution coefficient of phenol

Above a compound's pKa value, the molecule is almost completely dissociated, shedding a hydrogen ion and leaving an anionic molecule. The pKa values for B-naphthol and phenol are 9.51 and 9.89, respectively. At these high pH values, there is an abundance of hydroxide ions present. The water molecules congregate near these hydroxide anions. The smaller hydroxide ions are more strongly hydrated than the larger organic anions. The organic anions become less hydrated which allows them more freedom to move about and into the PFD phase. However, the decline in the hydration of the organic anion is less than would be expected from a neutral compound.

B. Extraction/Oxidation of B-naphthol

Adjustments of several variables were conducted to discern the physical and chemical phenomenon that occur in a two phase oxidation of B-naphthol. Measurements were made of the final B-naphthol concentration, the final TOC and the pH of the reacted system. Several intermediate peaks were also measured. The variables that were adjusted consisted of the initial pH of the water phase, the water to PFD ratio, the oxidation temperature, the shaking speed and the use of a copper catalyst. The pressure of the system was set by the oxidation temperature and was the saturation partial pressures of water and PFD combined.

1. The Effect of Initial pH

These experiments were performed at an oxidation temperature of 200 C and a water to PFD ratio of 2 to 6 by volume. The shaking speed was set at 200 rpm. The pH of the water was adjusted by adding a few drops of either concentrated nitric acid or sodium hydroxide to obtain a range of pH values. The initial water phase B-naphthol concentration was set at 500 mg/l.

Figure 6 shows the effect of initial pH on the disappearance rate of B-naphthol in the aqueous phase. The least amount of B-naphthol oxidation resulted from an initial pH of 6.2, while the two extremes of pH, (1.93 and 10.3) caused a much larger extent of oxidation. An initial pH of 8.9 produced a better result than a pH of 6.2 but less than the extreme pH values. Figure 7 shows a similar trend for the disappearance of TOC.

The order of these results corresponds well with the equilibrium distribution coefficients of B-naphthol of each pH. A larger value of the distribution coefficient produced a larger extent of oxidation. The initial pH values of 1.93, 6.20, 8.91, and 10.3 correspond to partition coefficients of 0.17, 0.020, 0.10 and 0.19, respectively.

The increased disappearance rate supports the fact that the oxidation reaction occurs in the PFD phase. Consider any rate mechanism, the disappearance rate of B-naphthol increases with an increase in the distribution coefficient if the reaction occurs in the PFD phase. On the other hand, if the oxidation reaction occurs in the water phase, an increase in the distribution coefficient results in a disappearance rate decrease.

Consider a kinetic controlled process, a larger distribution coefficient represents a larger concentration of B-naphthol in the PFD phase. This increased concentration boosts the oxidation rate in the PFD which consequently extracts more B-naphthol from the water phase. The same conclusion can be drawn for a diffusion controlled process, an increased distribution coefficient provides the system a larger driving force for mass transfer, increasing the disappearance rate of B-naphthol, thus no discrimination between model mechanisms can be deduced from this information.

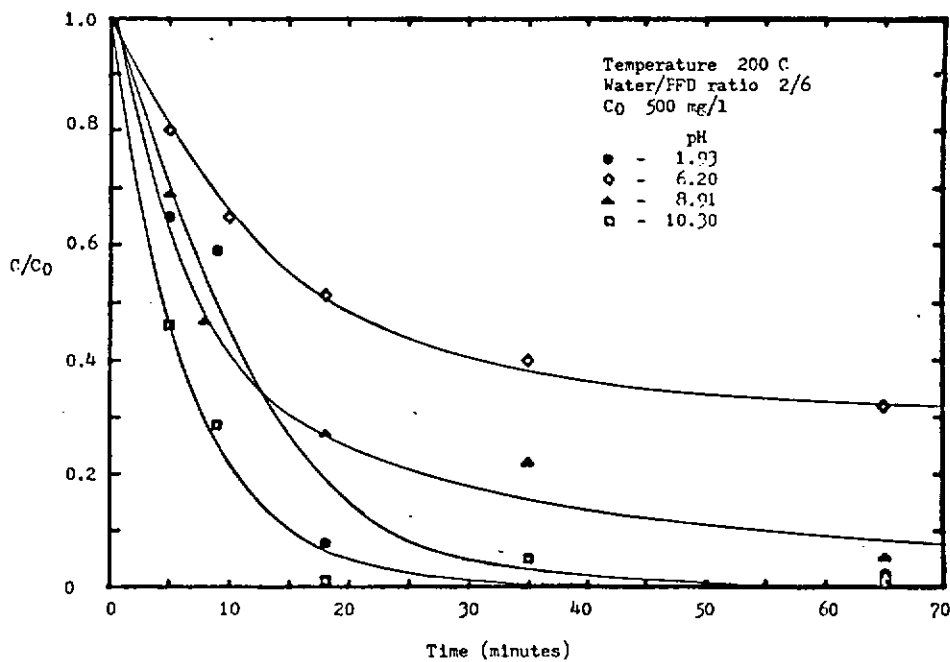


Figure 6 The effect of initial pH on the disappearance rate of B-naphthol

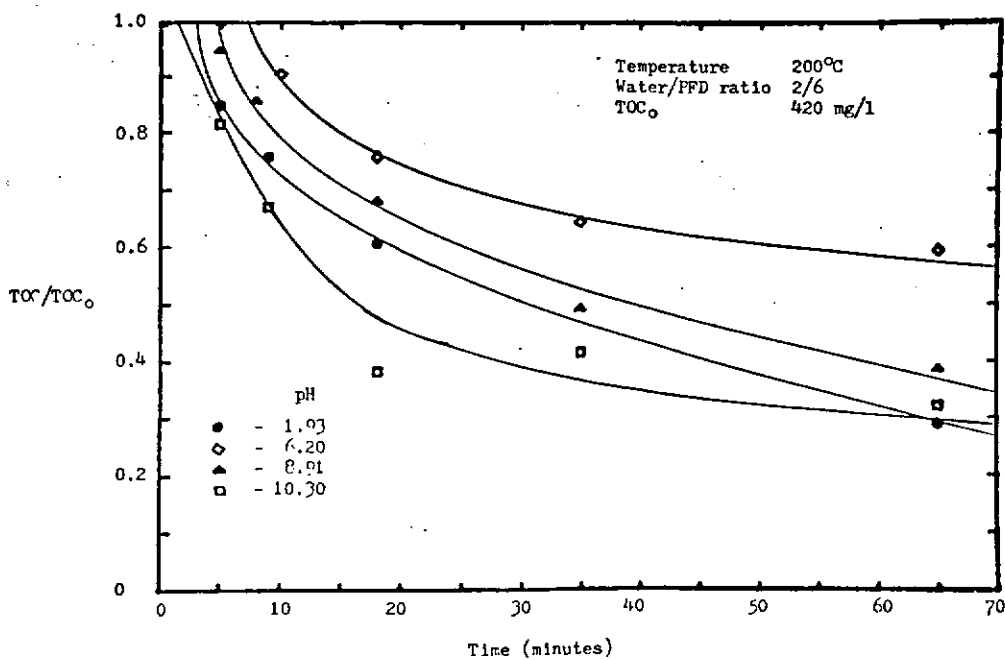


Figure 7 The effect of initial pH on the disappearance rate of B-naphthol TOC

The results of the initial pH effect on the disappearance of B-naphthol are directly linked to the change in the distribution coefficient. The pH values that yield the larger partition coefficient also show the faster decrease of B-naphthol. The TOC results indicate a similar trend due to the fact that most of it is the result of B-naphthol. The discrepancy between the two values indicates the formation of intermediates.

The disappearance rate of TOC is less rapid than that for B-naphthol. Figure 8 shows the change of the intermediate TOC over time for the various initial pH runs. The intermediate TOC is a calculated value obtained from the discrepancy between the carbon content of B-naphthol and the total TOC. It measures all intermediate product formation which is present in the water phase. The initial pH runs with the highest rate of reduction produced the largest quantity of intermediates. The large initial increase in TOC intermediates indicates the partial oxidation of the organic and is also observed as the lag phase in TOC reduction. The initial pH run of 6.2 showed the lowest amount of intermediate formation but it also showed the smallest B-naphthol and TOC reduction. All of the curves initially form a large amount of intermediates which slowly oxidized, further reducing the intermediate TOC. The leveling off and in some cases a slight increase indicate a resistance to further oxidation.

2. The Effect of the Water to PFD Ratio

These experiments were conducted at a temperature of 200°C and a pH of 8.9. The total volume of each sample was held constant at 8 milliliters. The water to PFD ratio was adjusted in ratios of 8/0, 3/5, 2/6, 1/7 and 0/8. The 8/0 ratio representing a one phase water system and the 0/8 ratio representing a one phase PFD system. All runs began with B-naphthol in the water phase except the one phase PFD system. In that one, the B-naphthol was dissolved directly into the PFD at a concentration of 200 mg/l.

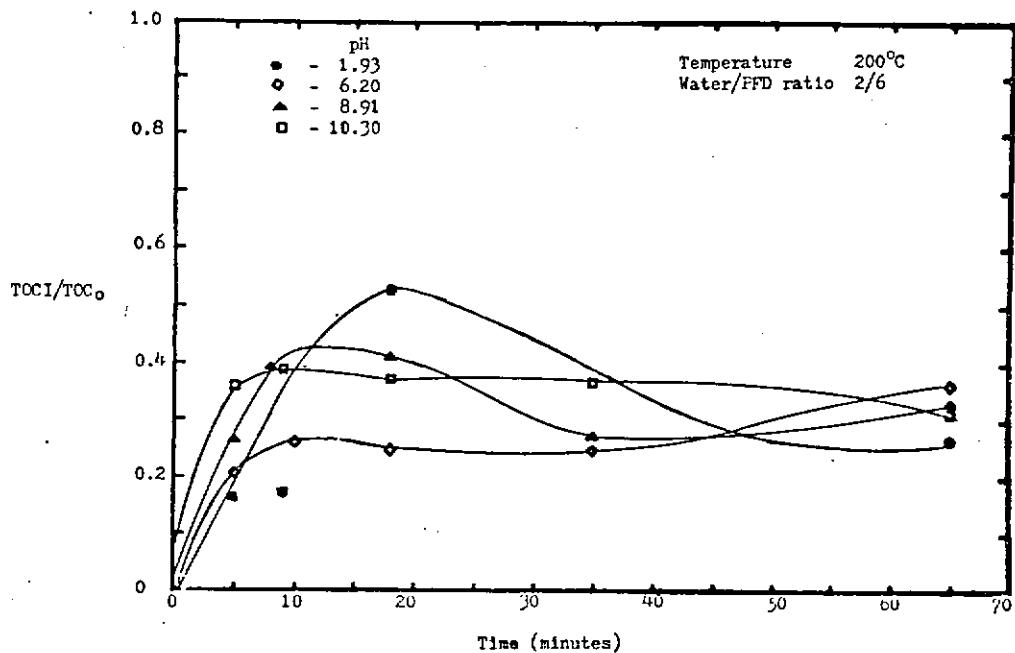


Figure 8 The effect of initial pH on the formation of intermediates from B-naphthol

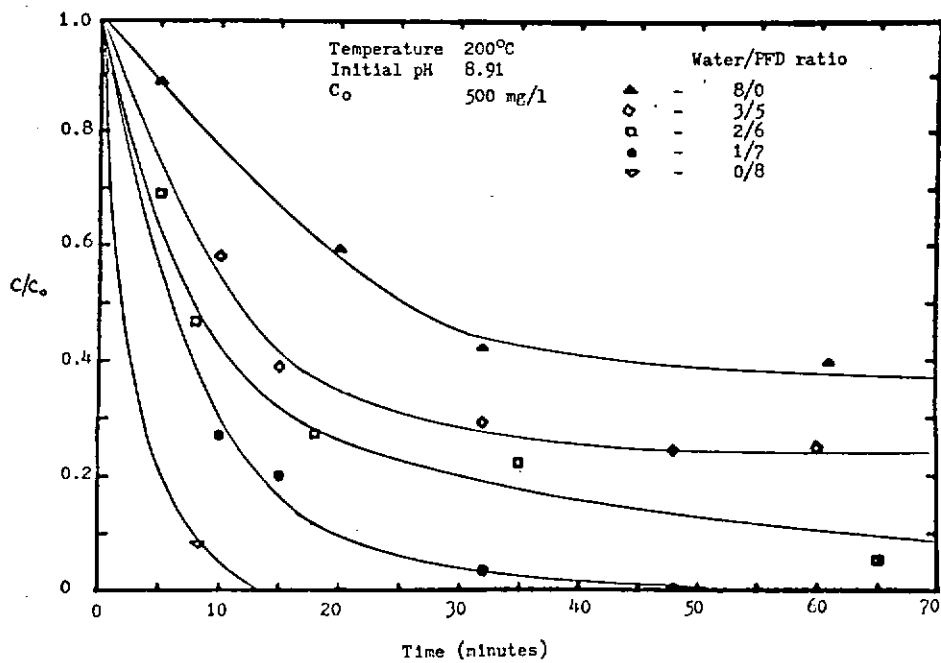


Figure 9 The effect of the water/FFD ratio on the disappearance rate of B-naphthol

The effect of the volume ratio caused a significant change in the disappearance rate of both B-naphthol and TOC. Figure 9 shows the effect of volume ratio on the reduction in B-naphthol. The reduction in TOC versus time for the change in the water to PFD ratio is shown in Figure 10. Both figures demonstrate that a decrease in the water to PFD ratio (increase in PFD volume) caused an increase in the rate of disappearance. This observation supports the earlier conclusion that the oxidation reaction occurs in the PFD phase, since the rate of disappearance would be constant or decrease if reaction occurred in the water with a decrease in the water volume. The comparison of the one phase oxidations show that the reaction kinetics are much faster in the PFD phase than in the water phase.

If the two phase system is controlled by the diffusion of B-naphthol into the reacting plane, then a change in the volume ratio should have no effect on the reduction of B-naphthol in the water phase. The rate of extraction is independent of the water to PFD ratio, as long as the interfacial surface area remains the same. Since the water to PFD ratio has a pronounced effect on the disappearance of both B-naphthol and TOC, the limiting case of a diffusion controlled process can be ruled out as a possible rate mechanism.

Assuming a kinetic controlled process, the extraction rate is fast compared to the reaction kinetics, the quantity of B-naphthol remaining in the water phase decreased with an increase in the PFD volume. At equilibrium, the water phase B-naphthol concentration is decreased to a level corresponding to the distribution coefficient. A water to PFD ratio of 2/6 results in a water phase concentration of 385 mg/l while a water to PFD ratio of 1/7 results in a concentration of 294 mg/l. But, the corresponding PFD phase concentration is also less for an increased PFD volume. Even though the oxidation rate in the PFD is slowed down by the decrease in the naphthol concentration, the quantity extracted from the water phase more than compen-

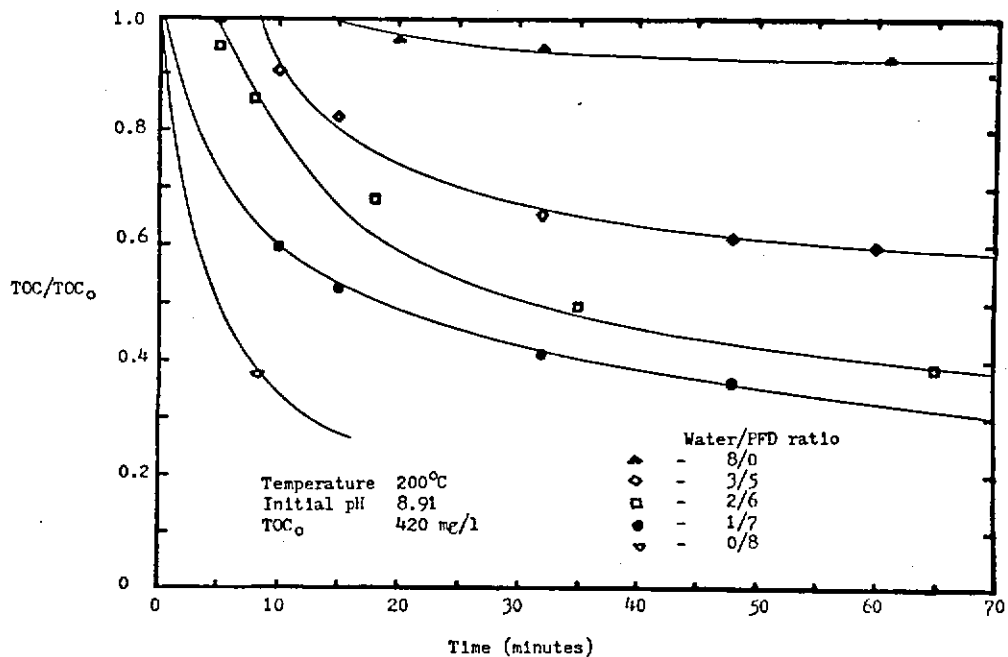


Figure 10 The effect of the water/FFD ratio on the disappearance rate of B-naphthol TOC

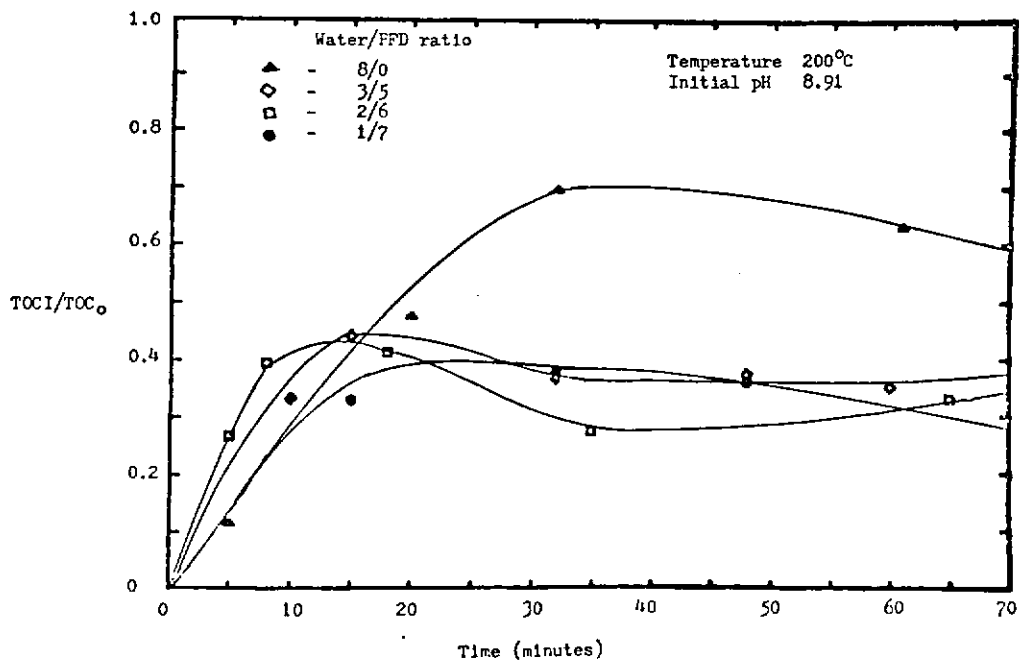


Figure 11 The effect of the water/FFD ratio on the formation of intermediates from B-naphthol

sates for this slow down. A decrease of 15 mg/l of the naphthol concentration in the PFD for a 3/5 ratio produces an additional 25 mg/l of naphthol in the water to extract into the PFD. A decrease of 10 mg/l of naphthol in PFD for a 2/6 ratio produces an additional 30 mg/l of naphthol in the water to be extracted into the PFD and a decrease of only 5 mg/l of naphthol in the PFD from a 1/7 ratio causes an additional 35 mg/l of naphthol in the water to extract into the PFD. Thus a decrease in the water to PFD ratio produces an increased disappearance rate for B-naphthol.

From the observations of the ratio plots, it is apparent that the results agree with the conclusions based on a kinetic controlled process. Thus, from these results the extraction/oxidation of B-naphthol appears to be controlled by the oxidation kinetics.

Figure 11 shows the effect of the water to PFD ratio on the TOC intermediate formation. The one phase water oxidation produced the largest amount of TOC intermediates. The two phase oxidations produced a more rapid initial increase in the formation of intermediates, but remained about one-half the amount of the one phase oxidation after about thirty minutes. The different intermediate profiles again indicate that the two systems oxidize the organic in two different phases, that is, the two phase system oxidizes the organic in the PFD phase. The largest intermediate quantity of the two phase oxidations resulted from the water to PFD ratio of 3/5. However, none of the ratios resulted in a drastic difference in the TOC intermediate formation.

An induction period was observed for most TOC results for B-naphthol as shown in Figures 7, 10, 12 and 15. All two phase TOC oxidations had shorter induction periods than the single phase. These induction periods indicate that B-naphthol is partially oxidized in the early stages.

3. The Effect of a Copper Acetate Catalyst

Figure 12 shows the effect of a copper catalyst on the disappearance rate of both B-naphthol and TOC. The introduction of the catalyst into the PFD phase produced an increased rate of disappearance for both measured quantities. Based on first order kinetic model, the ratio of the catalyzed kinetic constant over the uncatalyzed kinetic constant for B-naphthol was observed to be 2.18 and the same ratio for TOC was calculated to be 2.42. Thus, the introduction of 13.5 mg/l of Cu^{+2} in the PFD phase causes a 118% increase in the overall disappearance rate of B-naphthol and a 142% increase in the disappearance rate of TOC. Since the catalyst has no effect on the diffusion of the organics, the large increase in the disappearance rate indicates that the kinetics play a major role in determining the overall rate (kinetic controlled process).

Initially, all the copper is contained within the PFD phase. However, after eight minutes of oxidation, a third of the total copper catalyst was found in the water phase. It appears that copper equilibrates quickly between the two phases. This result indicated an enhanced oxidation of organics in both phases. Whereas, the water phase is unimportant for oxidation without a catalyst present, the presence of catalyst in the water phase increased the oxidation rate appreciably. Reaction in both phases caused, to some extent, the increase in the disappearance rate of B-naphthol and TOC.

The formation of intermediates for the catalyzed runs was determined to be greater than those for the uncatalyzed runs, based on the TOC difference. The reduction of B-naphthol is greatly increased by the introduction of a copper catalyst. This increased reduction formed more intermediates than the uncatalyzed runs did. Also, since it appears that reaction occurred in both phases, the lack of oxygen in the water phase caused more intermediates to be formed than would be formed if all oxidation occurred in the PFD phase.

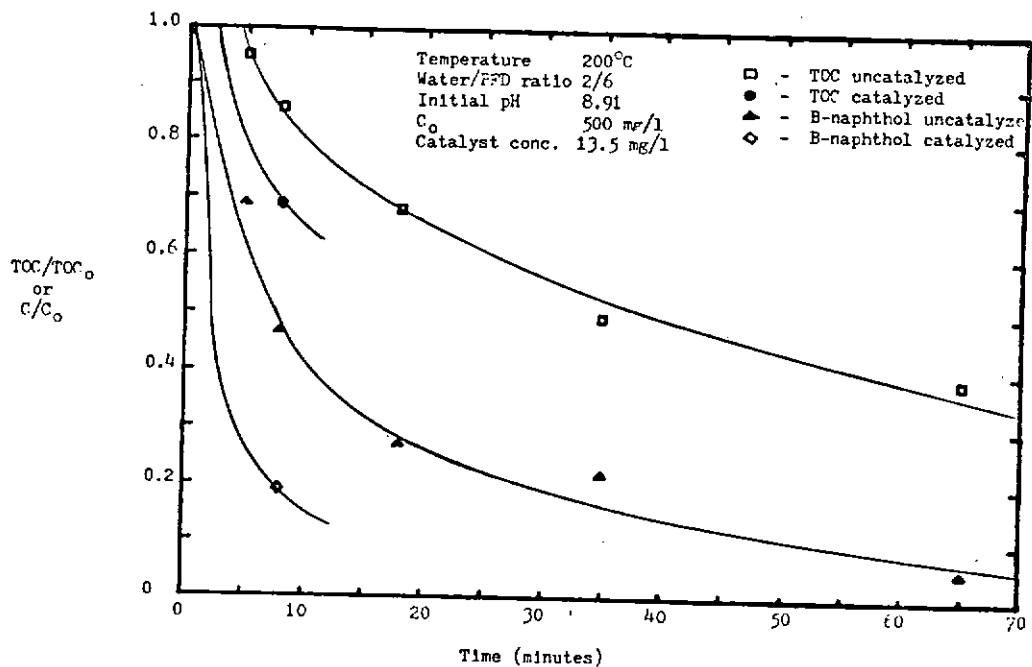


Figure 12 The effect of a copper catalyst on the disappearance rate of TOC and B-naphthol

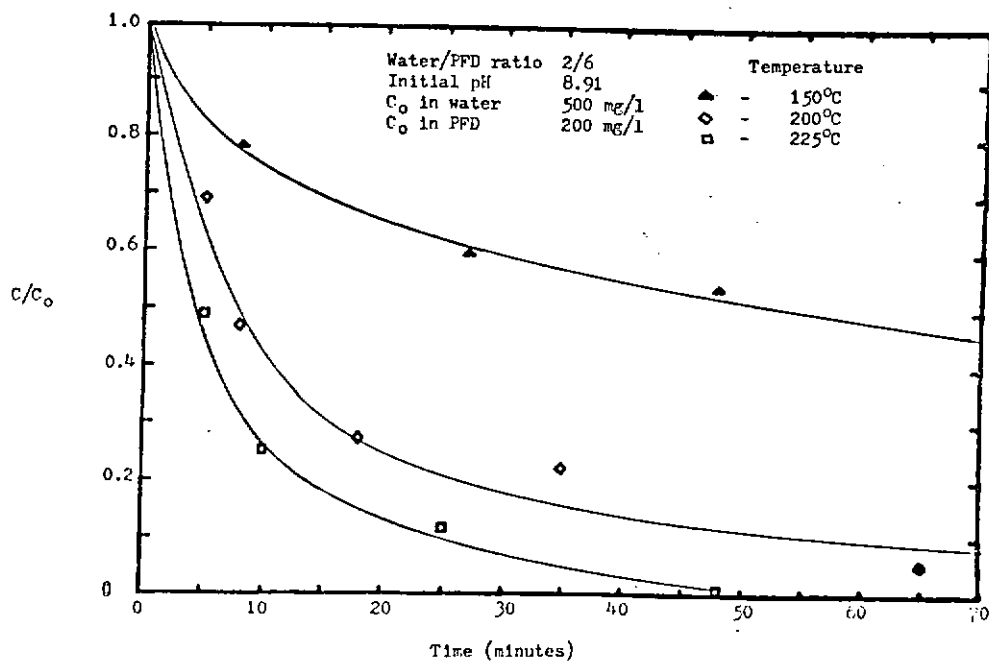


Figure 13 The effect of temperature on the disappearance rate of B-naphthol

4. The Effect of Temperature

Experiments were performed at temperatures of 150, 200 and 225°C. The corresponding saturation pressures were estimated to be 0.60, 1.90 and 3.10 MPa, respectively. The water to PFD ratios were set at 2/6 and 3/5 and the initial pH of the water was set at 8.90. All experiments were conducted according to the procedure for oxidation runs found in Chapter II.

Figure 13 shows the effect of temperature on the disappearance rate of B-naphthol for 150, 200, and 225°C. The kinetics increase exponentially as a function of temperature, diffusion is also enhanced by a temperature increase and by the pressure of the system. All of these cause the rate of disappearance for B-naphthol to increase as the temperature of the system is increased. The distribution coefficient may also be affected by the temperature similar to how Henry's constant changes with temperature.

The disappearance rate increased with an increased temperature, under any rate mechanism. The larger increase in the reduction of B-naphthol from 150°C to 200°C, as opposed to the increase from 200°C to 225°C, can be explained by the larger temperature increase, the tripling of pressure as opposed to a doubling and the possible change in the distribution coefficient.

The results of experiments performed at temperatures of 150 and 225°C are shown in Figure 14 for B-naphthol and Figure 15 for TOC. There are two curves at each temperature which represent the water to PFD ratios of 3/5 and 2/6. At 225°C, 99% of the B-naphthol is removed from the water phase, while at 150°C, only 38% of the B-naphthol is removed in 48 minutes for a water to PFD ratio of 3/5. The TOC curves demonstrate a similar difference between the two oxidation temperatures, however, their disappearance rates aren't as great as the B-naphthol disappearance rate because of the formation of intermediates.

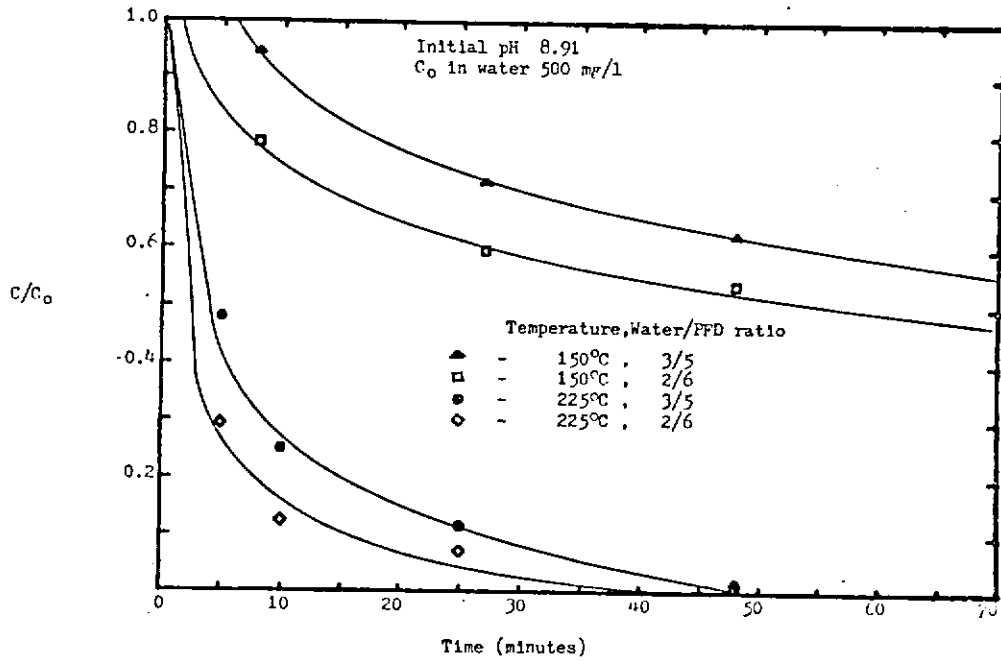


Figure 14 The effect of the water/FFD ratio on the B-naphthol disappearance rate at two different temperatures

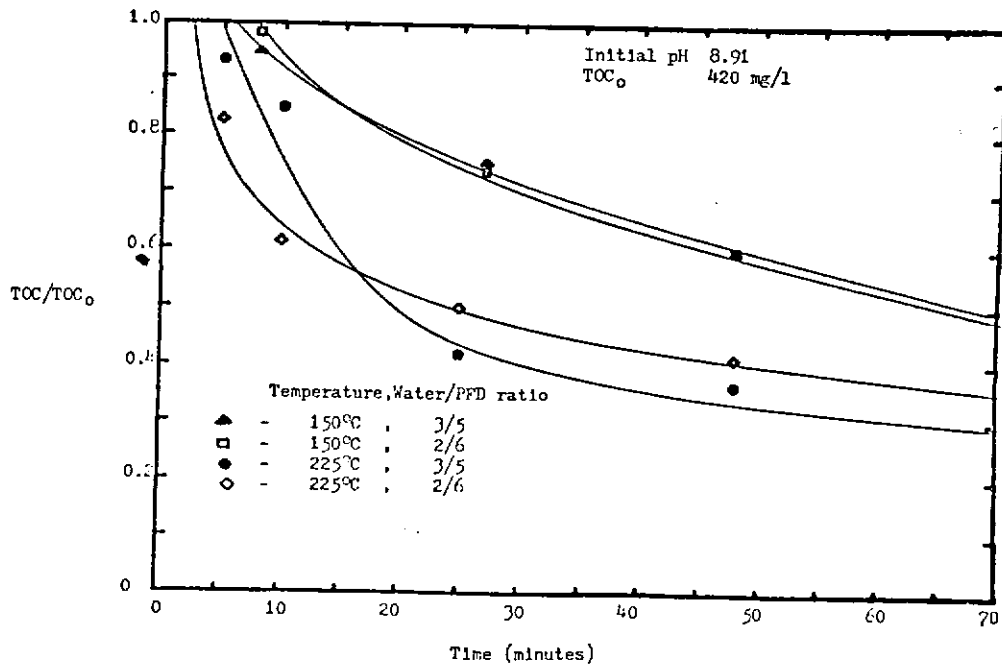


Figure 15 The effect of the water/FFD ratio on the TOC disappearance rate at two different temperatures

The results of the two phase oxidation at 150°C show a similar trend as those found at 200°C. A decrease in the water to PFD ratio (increase in the PFD volume) caused an increase in the disappearance rate of B-naphthol. An increased quantity of B-naphthol is extracted from the water phase with an increase in the PFD volume according to the distribution coefficient, yet the B-naphthol concentration in the PFD is less. Thus, initially the B-naphthol concentration in the water drops off due to extraction but then the rate of disappearance slows down. This scenario fits a kinetic controlled process and based on the observations, the oxidation of B-naphthol at 150°C follows a kinetic controlled model with oxidation occurring in the PFD phase.

The TOC disappearance rate of 150°C does not show a difference between the two water to PFD ratios. This indicates that the oxidation in the two ratios are producing different amounts of intermediates, that is, the 2/6 ratio produced more intermediates than the 3/5 ratio did. This result may be linked to the rates of diffusion and kinetics. At this lower temperature, intermediates formed in the PFD, quickly extract back into the water phase before they can be further oxidized in the PFD phase. Thus, the difference in TOC disappearance rates would be the same as observed at 150°C.

The water to PFD ratio has just the opposite effect at 225°C for the disappearance rates of both B-naphthol and TOC. The reduction rates decreased with a water to PFD ratio decrease. Thus the 3/5 ratio produced a better reduction than did the 2/6 ratio. The TOC plot was not as well defined as the B-naphthol profile. The 3/5 ratio produced a better reduction initially, however, after about 20 minutes the 2/6 ratio showed better results. This may be attributed to the smaller amount of oxygen present in the 3/5 ratio runs.

The extraction quantity of B-naphthol out of the water phase for the 2/6 ratio is greater than that for the 3/5 ratio, therefore, one would expect a better disappearance rate for the smaller water to PFD ratio. However, at these higher temperatures and pressures the oxidation of the organic is not entirely restricted to the PFD phase. Significant quantities of B-naphthol are oxidized within the water phase. With reaction occurring in the water phase, the disappearance rate of B-naphthol is enhanced by an increased water to PFD ratio.

The discrepancy between the disappearance rates of B-naphthol and TOC is attributed to the formation of intermediates. Figure 16 shows the TOC intermediate profiles for 150°C and 225°C at the different water to PFD ratios. The intermediate formation is the least for 150°C. This is partly due to the least amount of naphthol being consumed, but also to the most complete oxidation of the organic. The relative rates of diffusion and kinetics play an important role in the formation of intermediates. Generally, intermediates may form due to the lack of stoichiometric oxygen present in the reaction zone, at lower temperatures the reaction rate in the two phase system is slowed down, this allows more time for stoichiometric quantities of oxygen to diffuse into the reaction zone.

The formation of intermediates at 225°C represented the largest quantity formed of the three different oxidation temperatures. This is partly attributed to the greatest extent of oxidation of B-naphthol, but the significant oxidation of the organic in the water phase also plays a major role. The water phase oxidation is severely limited due to the lack of stoichiometric oxygen present in the water phase. The result being that more intermediates are formed in the water phase.

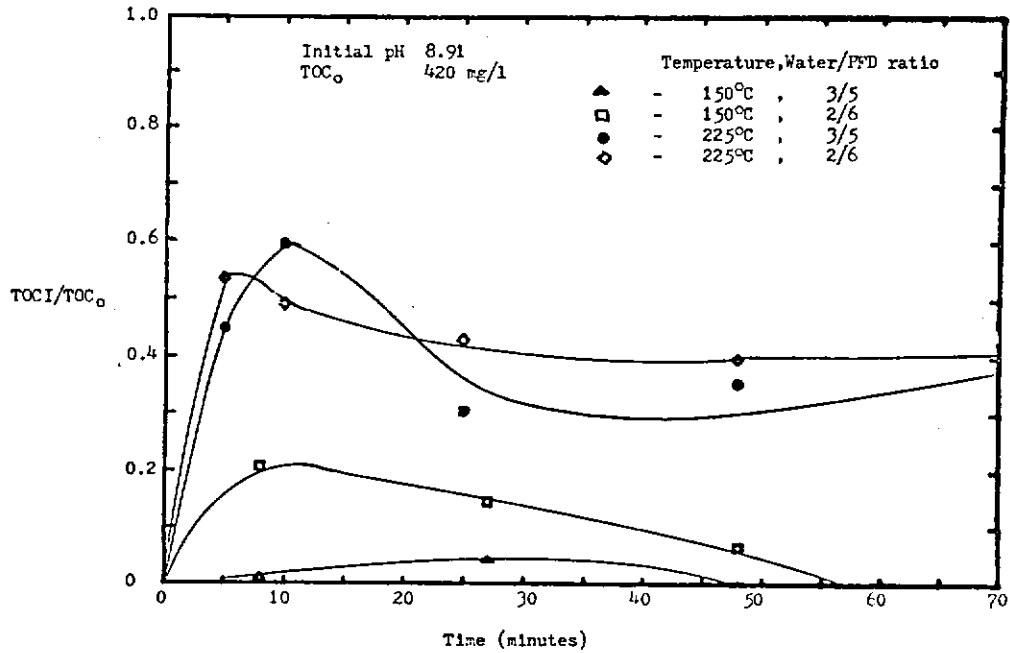


Figure 16 The effect of temperature and the water/FPD ratio on the formation of intermediates from B-naphthol

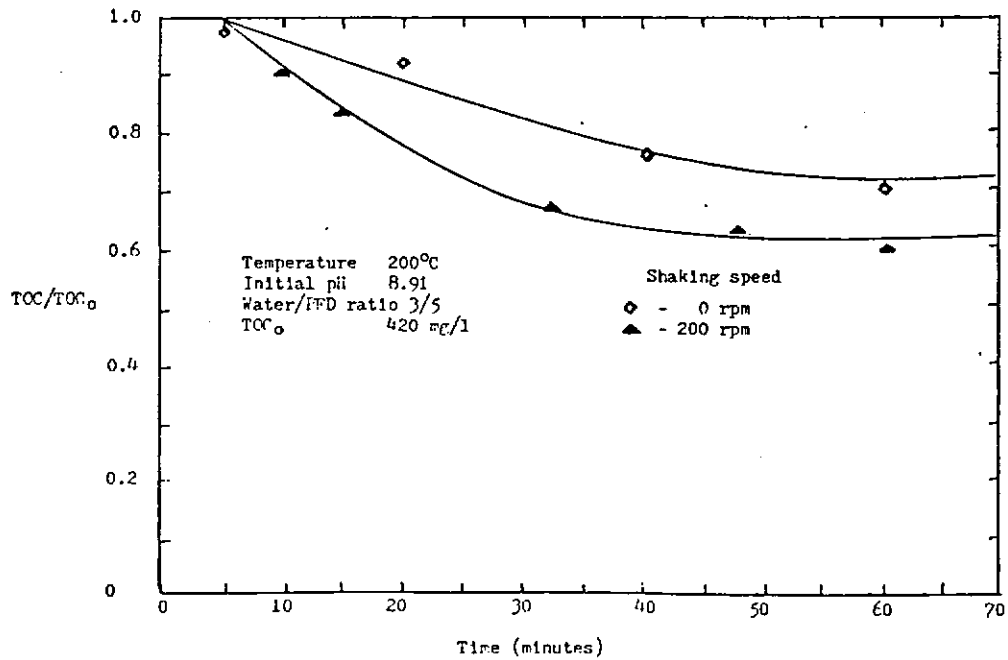


Figure 17 The effect of the shaking speed on the disappearance rate of B-naphthol TOC

5. The Effect of Shaking Speed

The extraction/oxidation of B-naphthol was affected by the apparatus shaking speed. As shown in Figure 17, the shaking speeds were set at zero and 200 rpm for several oxidation runs. The runs were conducted at an oxidation temperature of 200°C, a water to PFD ratio of 3/5 and an initial pH of 8.9.

The TOC disappearance rate increased with an increase in the apparatus shaking speed. The increased shaking speed caused more turbulence within the two phase and eliminated any large concentration gradients except in the liquid films. It also increased the interfacial surface area between the two phases. The results depicted in Figure 17 indicate that mass transfer of the organic plays a major role in the overall rate of disappearance. The amount of surface area affected the quantity of organic that diffused through the interface. Thus the relative rates of diffusion and kinetics must be considered in determining the overall reduction rate, a kinetic controlled process can be ruled out as the rate mechanism. Mixing must be provided to ensure an optimum amount of reduction in both B-naphthol and TOC.

6. The Formation of Intermediates

In several of the last sections, the TOC intermediates were presented as a function of time for the various parameter adjustments. The TOC intermediates were calculated from the discrepancy between the carbon content of the B-naphthol and the total TOC. Most of the plots depict an initial increase in the quantity of intermediates. As the concentration builds up, the curve reaches a maximum and begins to decrease over time. Over a longer period of time the quantity of intermediates remains constant. These intermediates resist further oxidation. The individual species are not identified in these analyzes.

Attempts were made to try and discern the identity of these intermediate compounds. Several peaks were consistently observed on the HPLC for most of the oxidation runs. A knowledge of the intermediate species for one phase oxidation have been determined by several investigators. They found several carboxylic acids, benzoic acids, aldehydes and phenol.

Table 3 lists the known compounds that were tested to determine if they were contained in our samples. The table also describes the specific retention times that were determined on the HPLC using the same technique. None of these compounds were found to elute at the same time as the unknown intermediates.

From the HPLC charts, it can be concluded that none of these known compounds tested were formed in detectable quantities during the two phase oxidation scheme. Since the intermediates formed in the two phase system are different than those formed during one phase oxidation, the oxidation reaction must be taking place in the PFD phase.

The intermediate peaks found by the HPLC for B-naphthol oxidation have retention times of 9.40, 25.7 and 27.3 minutes. B-naphthol has a retention time of 21.2 minutes. The longer retention times result from species that are either more nonpolar and/or have larger molecular weights. Thus, the two peaks at 25.7 and 27.3 minutes appear to be polymerized forms of B-naphthol which form due to the lack of oxygen present in the water phase. Both peaks have time profiles that reach a maximum in the early stages of oxidation and then decrease rapidly with time. Typical time profiles for the two peaks are shown in Figure 18.

The peak at 9.40 minutes has a lower molecular weight than it's parent B-naphthol. It appears to be a true intermediate resulting from the partial oxidation of B-naphthol. The peak increased linearly with an increase in the oxidation time. Figure 19 shows several typical time profiles of the 9.40 minute

TABLE 3
COMMON INTERMEDIATES FORMED DURING WATER PHASE OXIDATION

COMPOUND	MW	RETENTION TIME(MIN.)	SENSITIVITY (RFM)	REMARKS
Formic Acid	46.	2.9	10.0	Found in one phase oxidation of phenol
Succinic Acid	118.09	5.4	6.0	Phenol, Naphthol
Propanic Acid	74.08	4.5	25.0	One phase oxidation; naphthol
Fumaric Acid	116.07	3.2	5.0	Phenol
Maleic Acid	116.07	3.2	5.0	Phenol
Glycolic Acid	76.05	15.08	3.0	Phenol
Catechol	110.1	7.7	1.0	Phenol
Hydroquinone	110.1	4.7	1.0	Found in two phase oxidation of phenol
Lactic Acid	90.08	4.2	3.0	Phenol
Malonic Acid	104.06	3.4	5.0	Phenol
Acetic Acid	60.05	Not Retained	-	Phenol
Oxalic Acid	90.04	Not Retained	-	Phenol

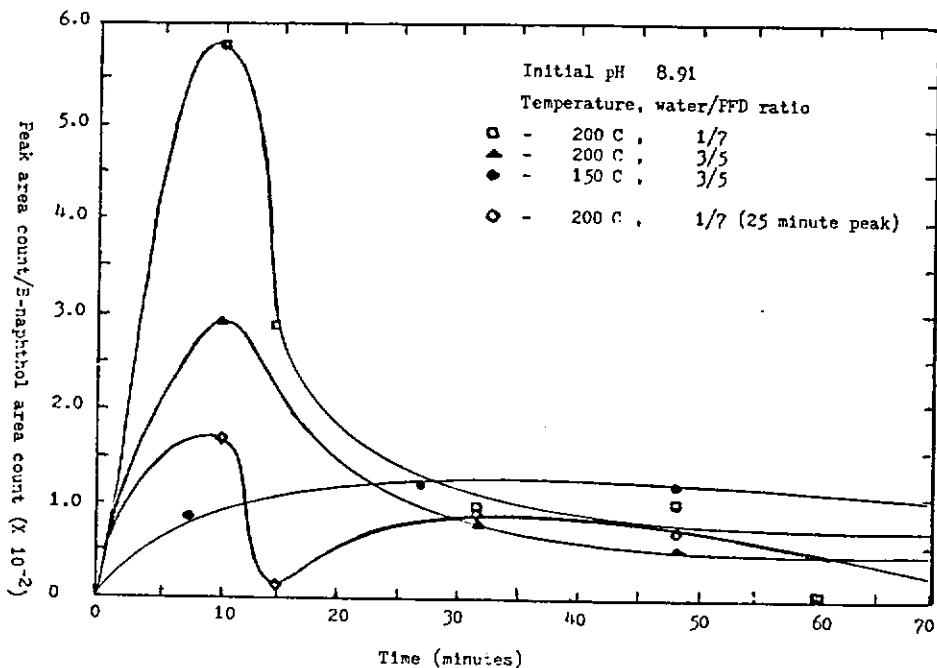


Figure 18 Time profiles of the 27.4 minute peak & one profile of the 25.0 minute peak on the HPLC from B-naphthol

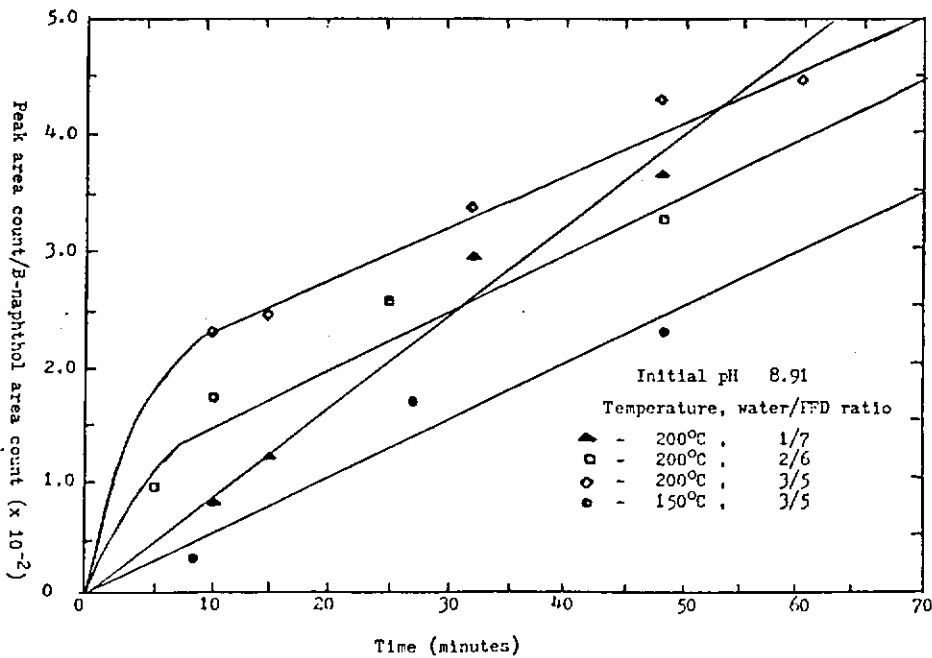


Figure 19 Time profiles of the 9.40 minute peak on the HPLC from B-naphthol

peak. It appears that this intermediate compound resists further oxidation, since it increased over time and did not reach a maximum. An analysis of this peak by the HPLC for ultraviolet wavelengths of 220 nm, 254 nm and 280 nm resulted in a decrease sensitivity, however, it did not disappear at the 254 nm wavelength which one would expect for an aromatic ring structure. This compound was suspected to be an acyclic aldehyde.

7. The Final pH

The final pH of each water sample was measured after the two phases had been separated. A plot of the final pH versus time is shown in Figure 20 for three oxidation temperatures.

The runs conducted at 150°C resulted in the smallest pH drop, while the 225°C runs produced the largest pH drop. The amount of the pH drop is directly related to the quantity of intermediates formed and the disappearance rate of B-naphthol. The decrease indicates that appreciable quantities of organic acids are formed in the two phase system. However, none of the suspected acids were detected by the HPLC.

C. Extraction/Oxidation of H-Coal Wastewaters

The H-coal wastewater was obtained from Ashland Oil's Cattlesburg Kentucky Plant during its full operation. The two phase oxidation conditions were set at a temperature of 200°C. A water to PFD ratio of 2/6 and an initial pH of 8.5. The wastewater contained several aromatic compounds including phenol, o-cresol hydroquinone and xylenol. Measurements were made of the TOC phenol and the final pH of the oxidized samples. A typical breakdown of the constituents of an H-coal wastewater is presented in Table 4. The original TOC was measured at 620 mg/l and the original phenol at 110 mg/l.

The results of the extraction/oxidation of H-coal wastewater are shown in Figure 21. The curves presented in the figure represent the profiles of TOC and phenol for the uncatalyzed runs and the profiles of TOC and phenol for the catalyzed runs. The uncatalyzed TOC profile exhibits an induction period of about five minutes and then proceeds to a total reduction of 52% of the original TOC in 90 minutes of oxidation. The catalyzed TOC

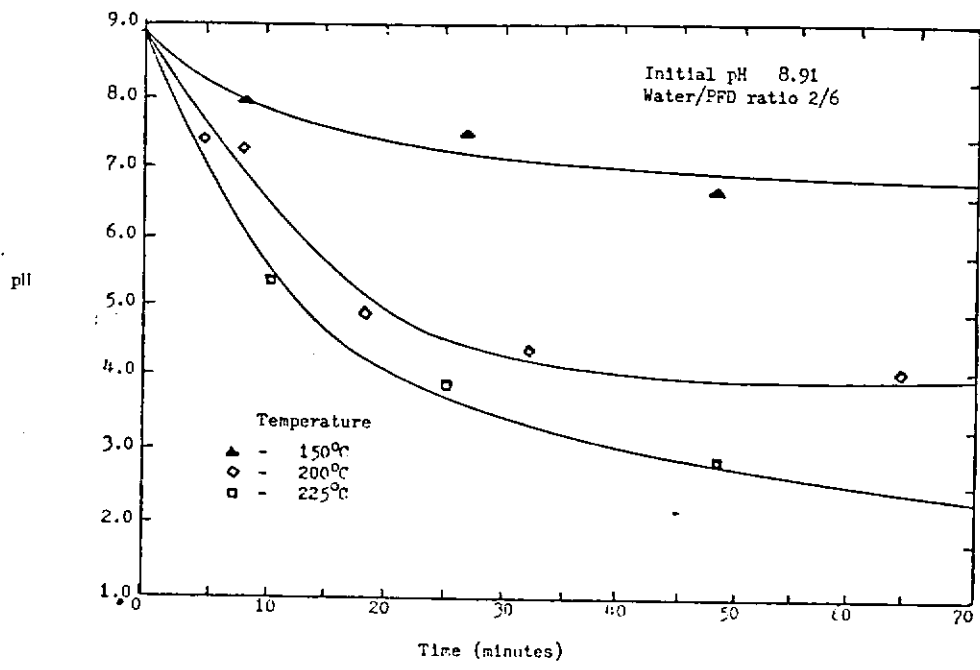


Figure 20 The change of pH for various temperatures from 2-naphthol oxidation

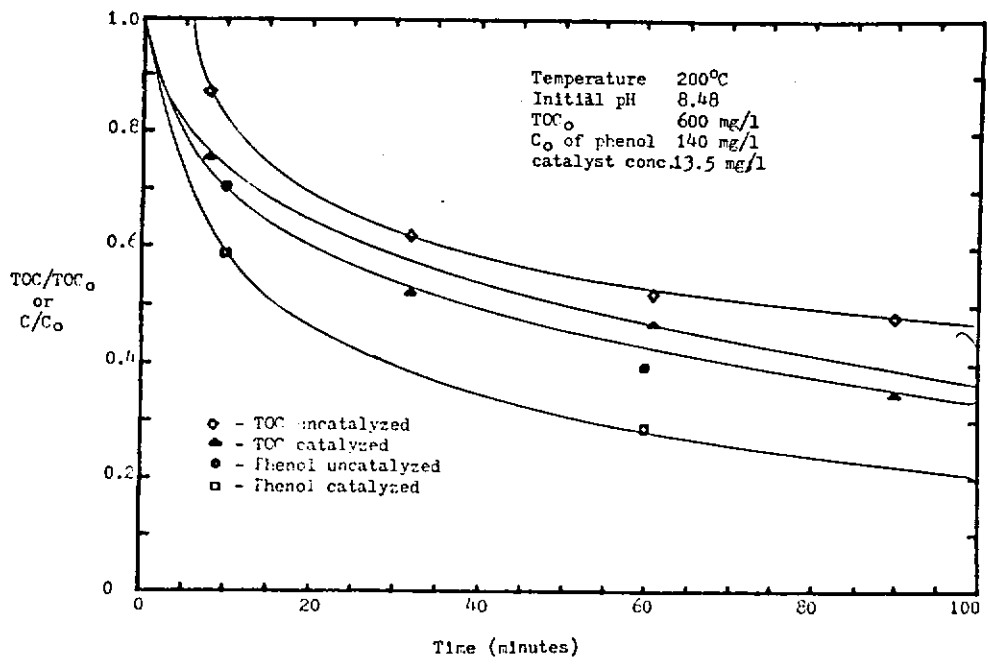


Figure 21 The two phase oxidation of H-coal washwater with copper catalyst

Table 4 Wash Water Characterization
(all values mg/l)

Parameter	Kentucky #9		Illinois #6
	Mean	Standard Deviation	One Sample
H ₂ S	8900	2300	10000
NH ₃	7600	2400	7000
Phenol	2300	460	3300
(p+m) Cresol	1200	180	1900
o-Cresol	410	55	660
Resorcinol	240	28	410
TOC	4900	1400	6900
TKN	7100	1700	7600
CN	27	18	8
Alkalinity	22000	8100	26000
TSS	29	21	26
TVSS	14	10	26
TDS	1500	1200	1500
Cl ⁻	1000	280	200
pH	9.4	0.4	9.5

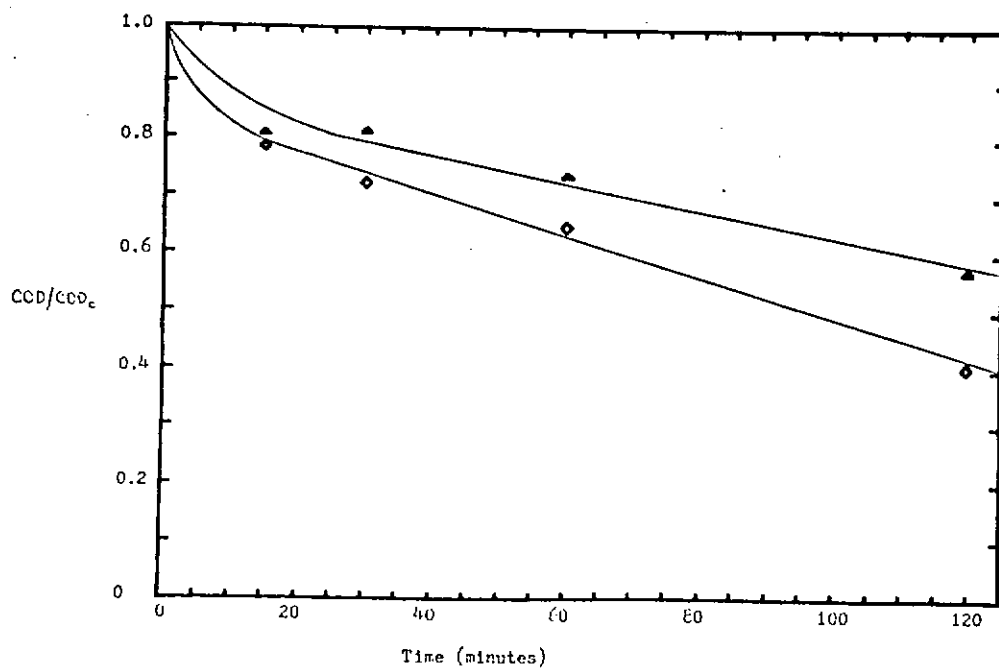


Figure 22 The one phase oxidation of H-coal washwater at two temperatures (3)

profile shows no induction period and quickly approaches 60% reduction in 60 minutes. The introduction of a copper catalyst into the PFD phase reduced the introduction time and increased the overall disappearance rate of the TOC. Initially all the catalyst was found in the PFD phase, however, after 10 minutes of oxidation, one-half of the catalyst was found in the water phase. After 60 minutes of oxidation, the copper catalyst was found to be in equilibrium between the two phases.

The copper catalyst increased the oxidation rate in the PFD phase but since it equilibrates quickly between the two phases, it also increases the oxidation rate in the water phase. Thus the increased disappearance rate is attributed to an increase in the oxidation rates of both phases.

The phenol profile shows a similar result with the introduction of a copper catalyst into the PFD phase. The increased reduction rate is not as pronounced an increase associated with the phenol solution shown in Figure 30 of thesis (32) (phenol section). This may be attributed to the slowing down of the mass transfer rate of phenol due to the interaction with other molecular species. The increased disappearance rate is caused by the increased oxidation rate of phenol in both phases. The water phase oxidation becomes significant with the transfer of copper catalyst from the PFD phase.

The oxidation of H-coal wastewater is improved by the two phase extraction/oxidation scheme. The time profile of the TOC of H-coal wastewater for a water phase oxidation is shown for two temperatures in Figure 22. Eventhough the one phase system operated at a higher pressure and a continuous supply of oxygen, the reduction rate of the two phase oxidation was faster than that for the single phase oxidation. The two phase system, at 200°C, approached the results found for the water phase oxidation of H-coal wastewater at 250°C. The initial rate of disappearance for the two phase scheme is much faster than either one phase system. The slowing down of the disappearance rate of the TOC may be caused by the lack of sufficient oxygen to completely oxidize the organic, as well as, the build up of intermediates that resist further oxidation.

The final pH of the two phase oxidation runs only showed a small decrease over the length of oxidation. After 90 minutes of oxidation, the pH of the uncatalyzed sample was measured at 8.10 while after 60 minutes the catalyzed sample pH was measured at 8.20. The small decrease in the pH of the water phase indicates that either very small amounts of acids were formed during the PFD phase oxidation or the H-coal wastewater has a buffering capacity to absorb large acid concentrations without changing pH.

D. Comparison of Results

1. Single Phase and Two Phase Oxidation Comparisons Between the Organics Tested

Single and two phase reaction schemes were performed on several organic constituents. Three single solute systems were investigated for the effect of several major parameters on their concentrations. The three solutes were B-naphthol, phenol and naphthalene. These compounds represented a wide variation in water solubility and from our initial testing, they also exhibited a large difference in distribution coefficients between water and PFD. The distribution coefficients were reported, earlier in this paper, as 0.103 for B-naphthol, 0.01 for phenol and 94.0 for naphthalene. These equilibrium values do not give us any information about the rates of mass transfer but they do indicate an availability of the organic within the PFD.

From an examination of the extraction/oxidation models, it is evident that the relative rates of mass transfer and chemical reaction are of the same order of magnitude. The reaction is enhanced by the extraction of the organic from the water phase, while the build up of the organic in the PFD increased the reaction rate. The oxidation of organics in the PFD phase is dependent on the mass transfer rate but is not directly dependent on the distribution coefficient. Thus, a prediction of the overall performance of this system on a single solute, cannot be based solely on the equilibrium distribution coefficient, since equilibrium may not be achieved by the system.

The oxidation of each organic in the water phase was performed to establish time concentration profiles. A comparison of the three organic concentration profiles are shown in Figure 23. All runs were conducted at 200°C in a sealed bomb and an initial supply of oxygen. The results indicate the degradation of the organic but do not represent the quantities that resulted in CO₂ and water.

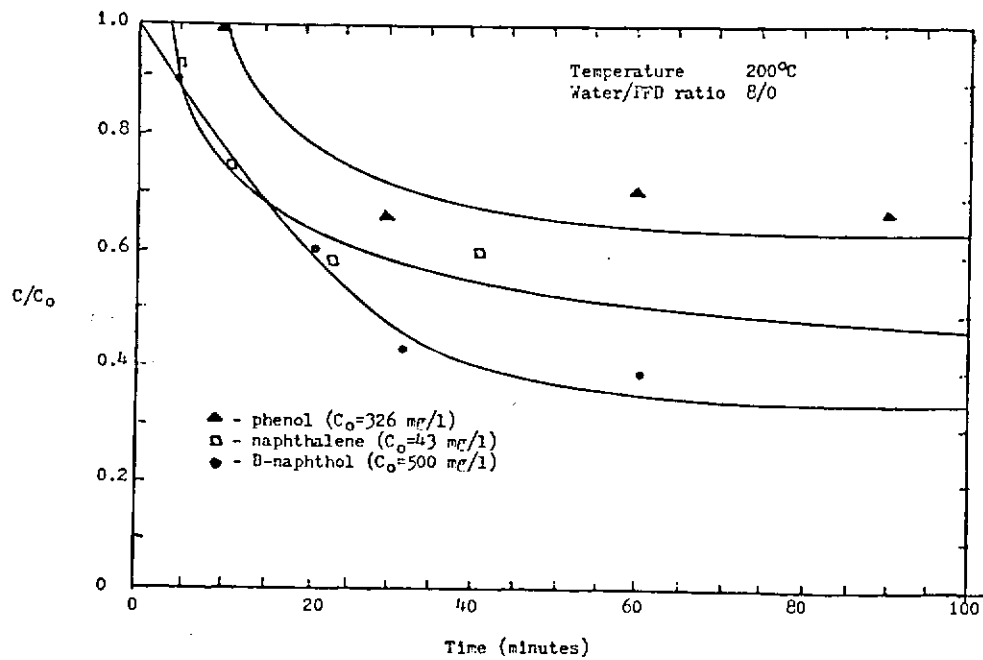


Figure 23 Comparison between the oxidation of organics in a water phase system

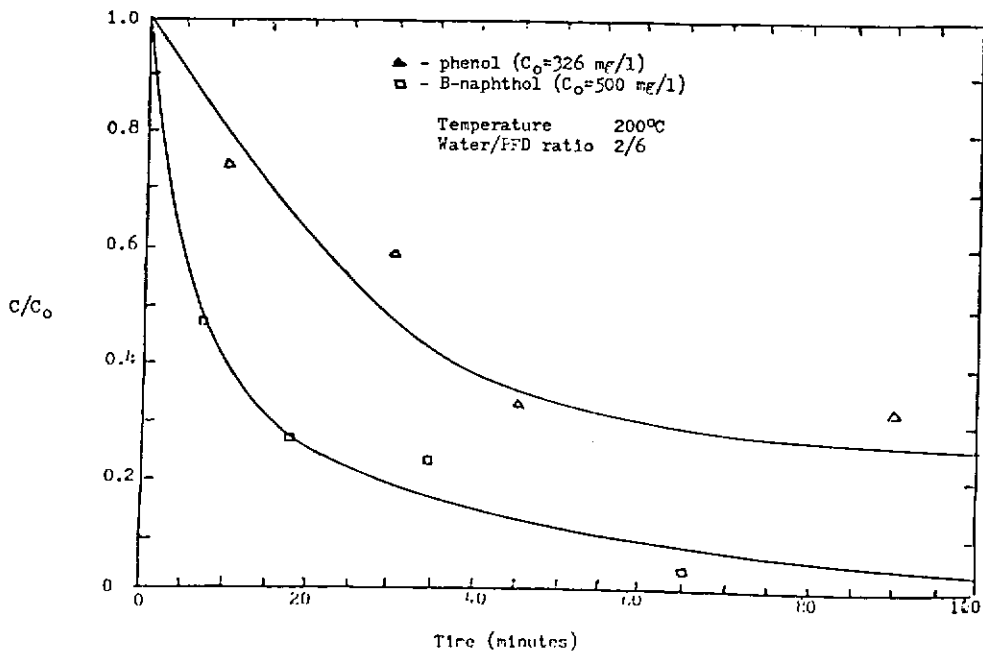


Figure 24 Comparison between the oxidation of organics in a two phase system

Phenol was found to oxidize the least of the three in the water phase system. There was an induction period of about 10 minutes for phenol followed by a period of rapid oxidation. The naphthalene profile also exhibited an induction period but it was less than 5 minutes long. The naphthalene oxidized quicker than phenol but was less oxidizable than B-naphthol, after about 15 minutes of reaction. The B-naphthol was oxidized the most of the three and did not exhibit an induction period.

The degradation of phenol is a slow process and requires severe reaction conditions to achieve a reasonable degree of reduction. The phenol molecule is highly stable at elevated temperatures and pressures. Thus, its relationship as the least oxidized organic results from the stable nature of the molecule and the high activation energy of reaction. Naphthalene and B-naphthol, in decreasing order, are less stable molecules at these reaction conditions. However, these compounds are not reduced to acceptable levels in the water phase.

An examination of Figure 24 shows that both phenol and B-naphthol reduction rate is improved through the introduction of the two phase system. Phenol is improved from a 35% reduction in the water phase oxidation to a 75% reduction in the two phase system. B-naphthol shows a similar change in reduction that is a 65% reduction in the water phase oxidation down to greater than 95% reduction in the two phase system. It is evident that the two phase system has a beneficial effect on the organic reduction, but what major parameter will help to determine the extent of this result? The distribution coefficient indicates the driving force for mass transfer across the boundary and therefore is an indicator of the mass transfer rate. However, information must be obtained concerning the mass transfer coefficient and the interfacial surface area, before a meaningful model can be established for this system.

Phenol has the lowest distribution coefficient of the three compounds and was also found to be the least reduced by the two phase system. B-naphthol proved to be readily oxidizable by the two phase system. Its distribution coefficient was determined to be ten times greater than that for phenol. From these results, the distribution coefficient does indicate the overall utility of this system, yet it does not provide the whole picture of what is going on in the system. The distribution coefficient should be used as a screening criteria to select other potential organics that can be oxidized readily by this system but it should not be the only criteria for selection of this process.

B-naphthol and naphthalene were oxidized in a PFD phase system, these are depicted in Figure 25. Directly dissolved into the PFD, the reduction rates of these compounds are vastly improved over the water phase oxidation scheme. The kinetic coefficient of B-naphthol in the PFD phase was determined to be almost 15 times greater than the kinetic coefficient in the water phase. Naphthalene shows a similar result, the kinetic coefficient in the PFD phase was found to be about 6.4 times greater than the kinetic coefficient in the water phase. These results demonstrate that oxidation occurring in the PFD phase was a much faster process.

In the PFD phase, both the organic and the oxygen are physically dissolved directly in the liquid phase. Both are in plentiful quantities and the oxidation proceeded without any mass transfer limitations. In the water phase, the oxygen concentration in the liquid phase is inherently below stoichiometric quantities, thus oxygen in the gas phase must transfer in the liquid phase before oxidation can proceed. It is evident that most organics will oxidize more easily in the PFD phase due to the abundant quantity of oxygen in the liquid phase.

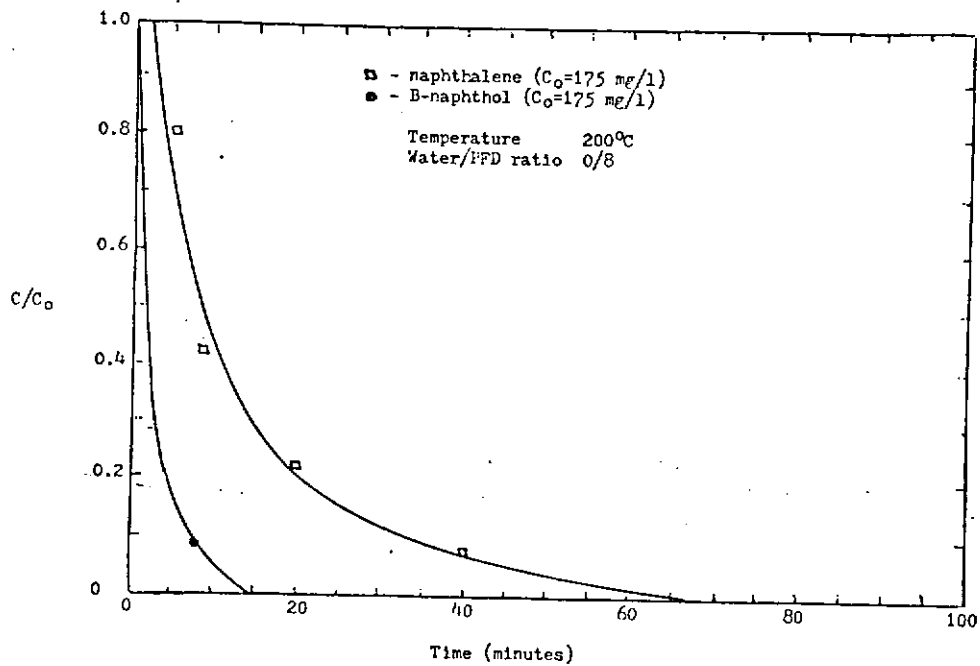


Figure 25 Comparison between the oxidation of organics in a FPD phase system

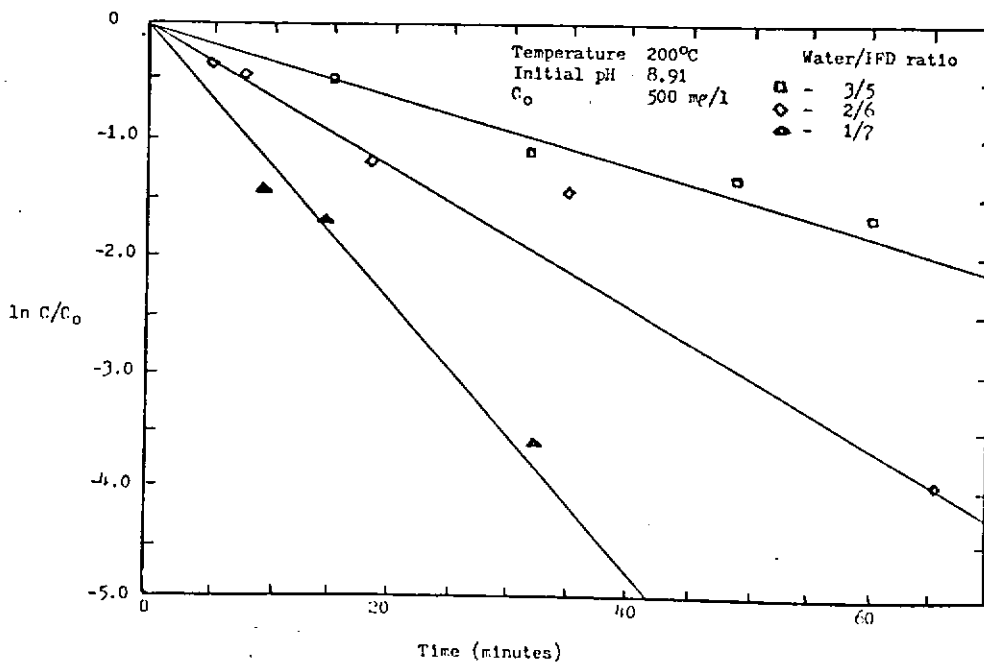


Figure 26 First order plots of B-naphthol oxidation runs

B-naphthol within the PFD phase was reduced by more than 99% in less than 15 minutes at a temperature of 200° C and an initial concentration of 175 mg/l. Naphthalene was reduced by about 99% in less than one hour of oxidation at 200° C. The order of the reduction rates was the same as that found in the water phase oxidation, thus a comparison of the water phase oxidation results, together with the equilibrium distribution coefficient, will enable one to predict the outcome of any other organic compound. Phenol was expected to be less oxidizable in the PFD phase than either naphthalene or B-naphthol, yet the reduction rate in the PFD would be improved over that found in the water phase.

2. Extraction/Oxidation Models

All of the experimental data was fit to a first order kinetic model with respect to the organic concentration. The equation is represented as:

$$\ln C_{AW}/C_{AW}^0 = -k't \quad (1)$$

A plot of $\ln \frac{C_{AW}}{C_{AW}^0}$ versus time yields a straight line with a slope of k' and a y-intercept of zero. Figure 26 depicts this plot for B-naphthol at 200° C, a pH of 8.9 and three water to PFD ratios. A best fit line was drawn through the experimental points to arrive at the smallest residual between the model and the experimental points. The slopes of these lines represent the overall disappearance rate coefficient which is a combination of the kinetic coefficient and the mass transfer coefficient. If the system was considered kinetic controlled, the constant would be expressed as the kinetic coefficient. A similar conclusion would be reached for a diffusion controlled process, namely, that the constant would represent the mass transfer coefficient. However, since this system is considered to be controlled by both mechanisms, the slope of the line represents a combination of the two coefficients.

Figures 27 and 28 show similar straight line plots for phenol and naphthalene, respectively. A list of the overall disappearance rate coefficients are found in Table 5 for these plots, along with the residual error between the model and the experimental points. It is evident from the residuals that the first order approximation is sufficient to predict the disappearance rate of the organics for most of our experimental runs. The TOC results did not show a consistently good correlation based on first order kinetics, therefore, no attempt was made to determine those coefficients.

An actual disappearance rate, depicted in Figure 29, for B-naphthol at 200°C and a 2/6 ratio, was compared with the first order plot using the coefficient from Table 5. The experimental plot shows an increased disappearance rate in the early stages of reaction over that predicted by the first order plot, but after about 30 minutes of reaction, the predicted disappearance rate increases over the experimental one. This seems to indicate that two regions of reaction occurred within the PFD phase. The second region is thought to be inhibited by the formation of intermediates, as well as the depletion of oxygen in the PFD.

The kinetic controlled process with reaction occurring in the PFD phase, was tested for each organic. This model was based on the assumptions that mass transfer was instantaneous between the two phases and the reactants followed one specific reaction path. With the use of two water to PFD ratio time profiles, this model determined the actual kinetic coefficient of the reaction and the distribution coefficient at the elevated temperatures. Using the two lower temperature kinetic coefficients, an activation energy of 5.7 kcal/mole was determined. This value is much lower than was expected according to other kinetic studies.

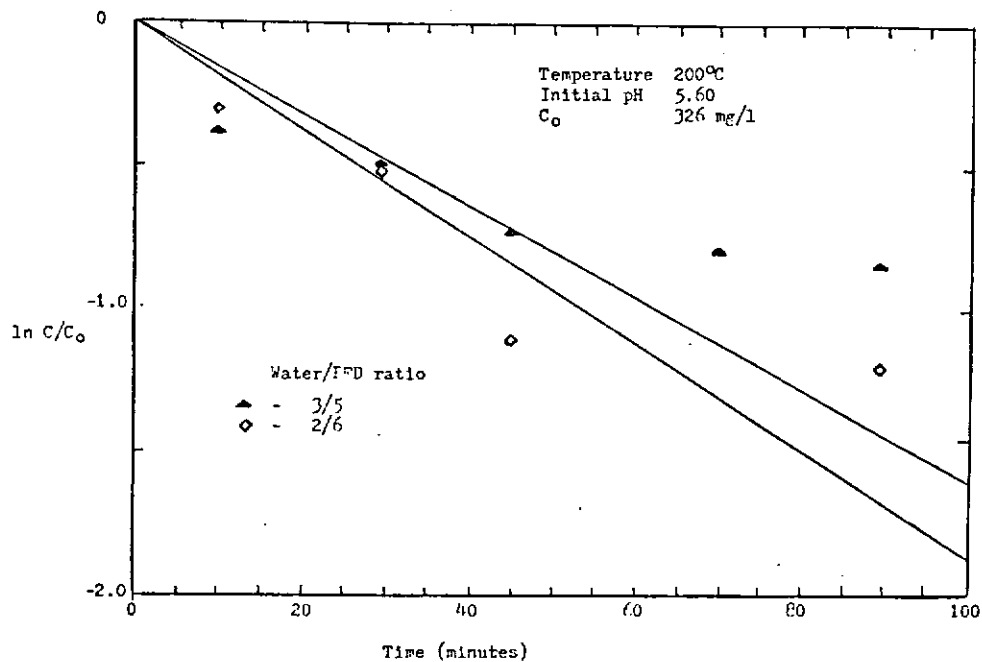


Figure 27 First order plots of phenol oxidation runs

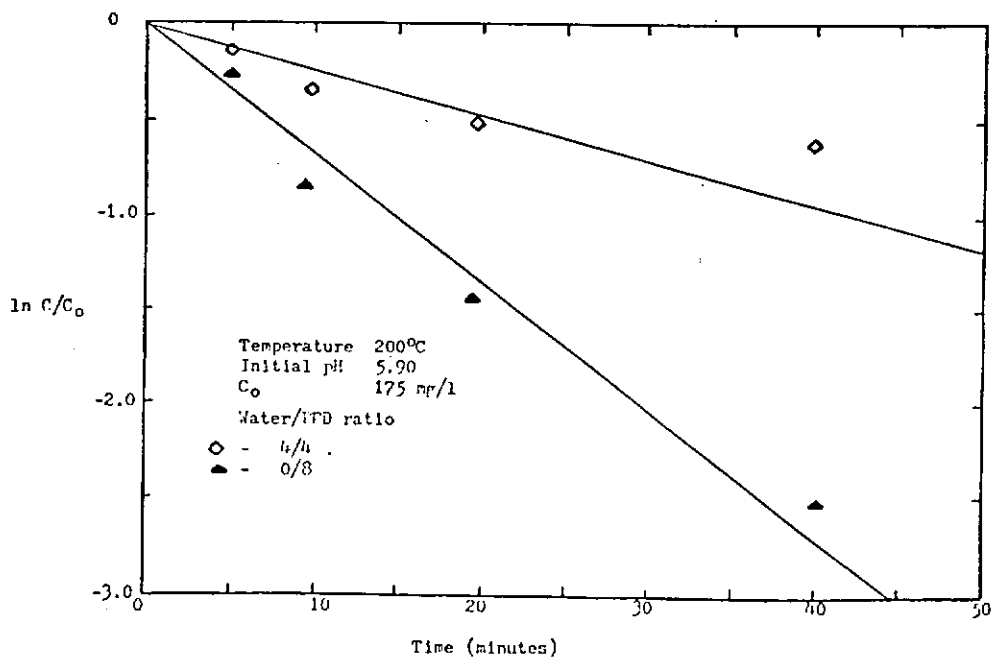


Figure 28 First order plots of naphthalene oxidation runs

TABLE 5

FIRST ORDER APPROXIMATION OF EXPERIMENTAL DATA

COMPOUND	TEMPERATURE (°C)	WATER/ FPD RATIO	pH	k ¹	R ²	# OF POINTS
B-naphthol	150	3/5	8.90	0.0090	0.953	4
B-naphthol	150	2/6	8.90	0.0157	0.937	4
B-naphthol	200	3/5	8.90	0.0370	0.979	6
B-naphthol	200	1/7	8.90	0.1154	0.955	5
B-naphthol	200	0/8	--	0.316	1.00	
B-naphthol	200	8/0	8.90	0.0212	0.927	6
B-naphthol	200	2/6	8.90	0.0571	0.943	6
B-naphthol	200	2/6	6.20	0.0346	0.923	6
B-naphthol	200	2/6	10.3	0.127	0.952	6
B-naphthol	200	2/6	1.93	0.0734	0.981	6
B-naphthol	225	3/5	8.90	0.112	0.872	5
B-naphthol	225	2/5	8.90	0.102	0.895	5
B-naphthol (catalyzed)	200	2/6	8.90	0.124	1.00	
Phenol	200	3/5	5.60	0.0133	0.854	6
Phenol	200	2/6	5.60	0.0233	0.877	5
Phenol	200	8/0	5.60	0.0050	0.921	4
Phenol	250	3/5	5.60	0.0611	0.759	5
Phenol	250	3/5	1.90	0.0511	0.857	5
Phenol	250	3/5	10.1	0.0495	0.921	
Phenol (catalyzed)	200	3/5	5.60	0.0438	1.00	
Naphthalene	200	4/4	5.90	0.0250	0.962	5
Naphthalene	200	0/8	--	0.0638	0.946	5
Naphthalene	200	8/0	5.90	0.0099	0.925	5

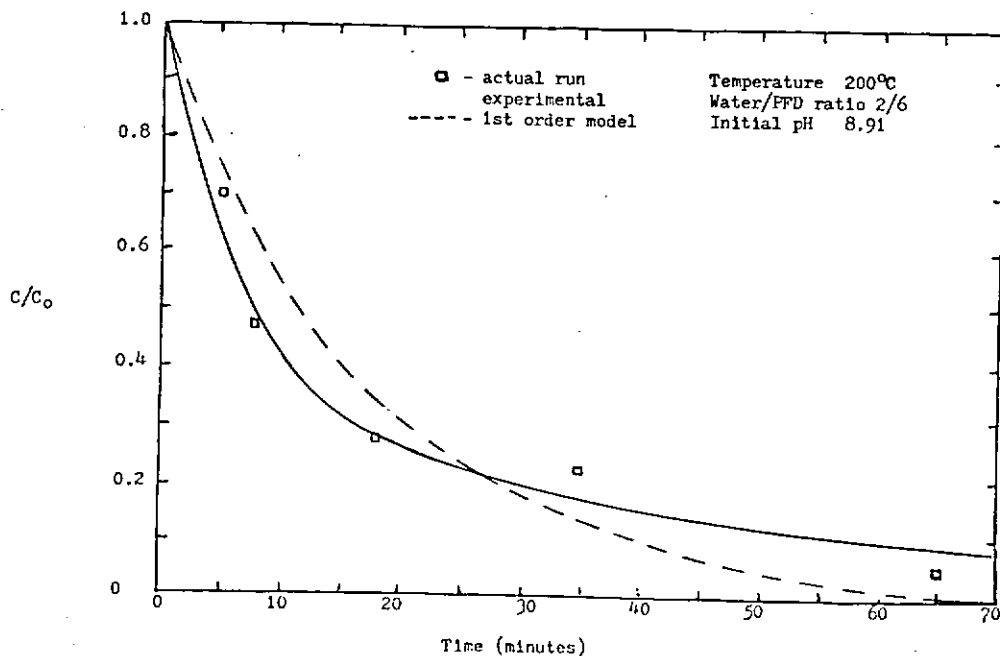


Figure 29 Comparison between the first order model and the experimental run

This model does not fit the experimental data for B-naphthol. The low value of the activation energy indicates that the true kinetics are not being represented by this model approach. Also, the distribution coefficient for the 225° C runs, was calculated as a negative number yet it is inherently positive.

The results obtained for the other organic compounds cannot be ruled out strictly on their values, however, the distribution coefficients appear to be quite different from their ambient equilibrium values. Mass transfer has been found to be an appreciable part in the determination of the overall disappearance rate. These systems are not kinetic controlled processes, therefore this model has been ruled out as a possible rate mechanism.

Using the true kinetic coefficient of B-naphthol oxidation in the single PFD phase, the values of the distribution coefficients at the oxidation temperatures were determined, based on the kinetic controlled model of Equation 1. They are depicted in Table 6. The change in the values indicates a dependency of the distribution coefficient on temperature. Eventhough this model has been ruled out as a rate mechanism, this result does indicate an effect of temperature on the distribution coefficient.

An attempt was made to dissect the components of the disappearance rate coefficients found in Table 5 into kinetic and mass transfer components according to the following equation:

$$\frac{1}{k'} = \frac{\alpha}{k_p' k_s a} \quad (2)$$

Where α is a constant of the system. The true kinetic coefficient is known from the experimental results of B-naphthol at 200° C. The change of the mass transfer coefficient and surface area together can be expressed as a ratio of two water to PFD ratio values. The mass transfer term for the 2/6 water to PFD ratio was 55% greater than the 3/5 water to PFD ratio mass transfer term. The 1/7 water to PFD ratio resulted in a mass transfer

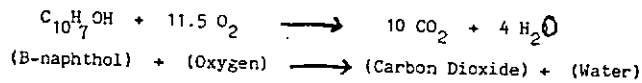
TABLE 6

PREDICTED DISTRIBUTION COEFFICIENTS OF B-NAPHTHOL
AT THREE TEMPERATURES

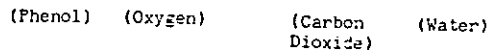
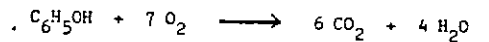
TEMPERATURE	K_p^1	D
150°C	0.054	0.129
200°C	0.316	0.078
225°C	0.671	0.061

TABLE 7

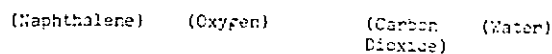
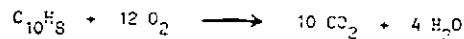
OXYGEN REQUIREMENTS FOR EACH ORGANIC



WATER/PFD RATIO	INITIAL CONC. (PHASE) (mg/L)	QUANTITY OF ORGANIC (m moles)	OXYGEN REQUIRED (m moles)	OXYGEN PRESENT (m moles)	PERCENT OF STOICHIOMETRIC
8/0	500 (water)	2.77×10^{-2}	3.19×10^{-1}	6.67×10^{-3}	2.2%
3/5	500 (water)	1.04×10^{-2}	1.20×10^{-1}	8.18×10^{-2}	67.0%
2/6	500 (water)	6.94×10^{-3}	7.98×10^{-2}	9.82×10^{-2}	123%
1/7	500 (water)	3.47×10^{-3}	3.99×10^{-2}	1.15×10^{-1}	288%
0/8	200 (PFD)	1.11×10^{-2}	1.28×10^{-1}	1.31×10^{-1}	102%



8/0	326 (water)	2.78×10^{-2}	1.95×10^{-1}	6.0×10^{-3}	3.1%
3/5	326 (water)	1.04×10^{-2}	7.28×10^{-2}	8.18×10^{-2}	112%
2/6	326 (water)	6.91×10^{-3}	4.84×10^{-2}	9.82×10^{-2}	203%



8/0	42 (water)	2.63×10^{-3}	3.16×10^{-2}	6.0×10^{-3}	19.0%
4/4	175 (PFD)	5.47×10^{-2}	6.56×10^{-2}	6.55×10^{-2}	100%
0/2	175 (PFD)	1.09×10^{-2}	1.31×10^{-1}	1.31×10^{-1}	100%

term that was 211% greater than the 3/5 water to PFD ratio one and 100% greater than the 2/6 water to PFD ratio mass transfer term.

The diffusion controlled process with instantaneous reaction was examined for a fit with the experimental data. This model assumed that the rate of diffusion into the PFD phase determined the overall disappearance rate. A reaction plane was assumed to exist where both reactants reach zero concentration. According to this model, the mass transfer coefficient and the distribution coefficients determine the overall rate. Unfortunately, we do not have enough data to perform the nonlinear analysis needed to estimate the parameters of this model. Also a knowledge of the unequilibrated organic concentration in the PFD phase could not be measured.

From the observations made during the oxidation runs, the volume of the reaction phase profoundly affected the overall disappearance rate. This fact, together with the knowledge that the reaction rate is finite, indicated that this overall disappearance rate is determined by both the mass transfer of reactants and the reaction kinetics of this system.

Under the circumstances stipulated in the preceding paragraph, the mathematical model that best represents the water/PFD reacting system is one which incorporates both the mass transfer and reaction kinetic parameters. The model of Equation 1 satisfied this condition, and is therefore considered the best fit model, even though no data analysis can confirm this finding. Sharma found this model fit reaction systems where both the mass transfer rate and the reaction kinetics rate played a role in determining the overall disappearance rate.

The important parameter in this model is the enhancement factor. Pure mass transfer is enhanced by the disappearance of the build up concentration due to reaction. Information must be gained about the magnitude of both the reaction kinetic coefficient and the mass transfer coefficient. This will enable the enhancement factor to be calculated.

E. Membrane Separation Results

The use of membrane processes for waste purification and concentrate volume reduction is gaining considerable attention in many industries. For hazardous wastes containing metals and priority organics, reverse osmosis membranes can provide simultaneous separation of both inorganics and organics. The recent industrial development of non-cellulosic (aromatic polyamide, sulfonated polysulfone, etc.) thin-film composite membranes has provided treatment techniques with high solute (metal salts and organics) separations (even at low pressures of 200-300 psi), and insignificant compaction problems. The low pressure reverse osmosis membranes have definite advantages in terms of energy savings, and capital cost. The composite membranes perform better than cellulose acetate membranes in almost all aspects, including water flux, rejection, temperature and pH stability, and pressure requirements. This project deals with the use of low pressure membranes for the concentration of hazardous wastewaters.

Any membrane process produces two streams: a permeate stream and a concentrate stream. The process is generally evaluated in terms of two parameters: membrane rejection, R (or permeate solute concentration, C_p) and water flux J_w . The solute-rejection parameter is defined as

$$R = 1 - \frac{J_s}{J_w C} = 1 - \frac{C_p}{C} \quad (3)$$

in which J_s is the solute flux, C_p and C are the permeate and feed solute concentrations, respectively. With synthetic thin-film composite membranes the skin (barrier layer) and porous substructure are made of two different noncellulosic polymers. Low pressure operation reduces the energy cost significantly.

Membrane rejection of solutes is a function of the extent of distribution of the solute between the solution and membrane phases. Various factors affect solute distribution: solute solubility and polarity, functional group, solute branching, solution pH (solute ionization), and temperature.

Membrane studies were conducted with model compounds and with actual

wastewaters. Rejections of phenolic compounds increased with increasing solution pH for both membranes. Naphthalene, a polynuclear aromatic hydrocarbon, was removed more efficiently (96% rejection) at low pH (5-8) values than any other compound tested. Organic solute rejections (Figure 30) of unionized (at low pH) compounds are in the order: phenol (rejection = 77%) < resorcinol and catechol < 0-cresol < 2-naphthol < naphthalene (rejection = 96%) (high-pressure membranes). Maximum rejections were established at high pH (10-11) for phenol, 0-cresol, and 2-naphthol for both membranes. Rejections for the low-pressure membrane were 68% phenol and 84% 2-naphthol. Rejections for the high-pressure membrane were 96% phenol, 98% 0-cresol, and 97.5% 2-naphthol. Correlations of membrane solute rejections with physiochemical parameters such as polarity (Hammett and Taft parameters) and aqueous solubility showed increased rejections of unionized solutes with decreasing solubility or polarity.

We have also conducted extensive work with actual coal liquefaction wastewater with thin-film aromatic polyamide (FT-30) spiral wound modules. This highly colored wastewater (biotreated H-coal water) contained NaCl (1600 mg/l), TOC (80 mg/l), trace heavy metals, etc., and membrane permeate results showed NaCl at 120 mg/l, TOC < 2 mg/l, and Cu, Zn at < 0.01 mg/l. Individual HPLC results of TOC showed 92-95% rejections of organic acids (maleic, formic, etc.) and 100% rejections of color organics (valerolactam, methylpiperidinone, etc.). Standard salt rejection (even after one year operation) stayed constant at 97.4%, demonstrating excellent membrane stability. Membrane separation with non-biotreated water (Table 4) also showed effective removal of phenolic and inorganic constituents. For example, even at 5x concentration factor the rejection of phenol was 90.5% and the rejections of cresol and resorcinol were 93-95%.

Preliminary experiments (FT-30 membrane) were also conducted with short chain organic acids (at 8 millimolar concentration) and with an actual pond water from pesticide manufacturing operations. With organic acids (formic, propionic, butyric) the rejections (at pH = 5, i.e., pH > pK_a) were 99.4 to 99.9%. The successful treatment of dilute pesticide wastes (TOC = 120 mg/l, chloride = 1600 mg/l, Na⁺ = 1400 mg/l, Cu, As, Zn = 0.5 - 3 mg/l, conductivity = 8400 µmho/cm, etc.) was also demonstrated with a 99.6% salt rejecting FT-30 membrane. At 340 psi and 90% water

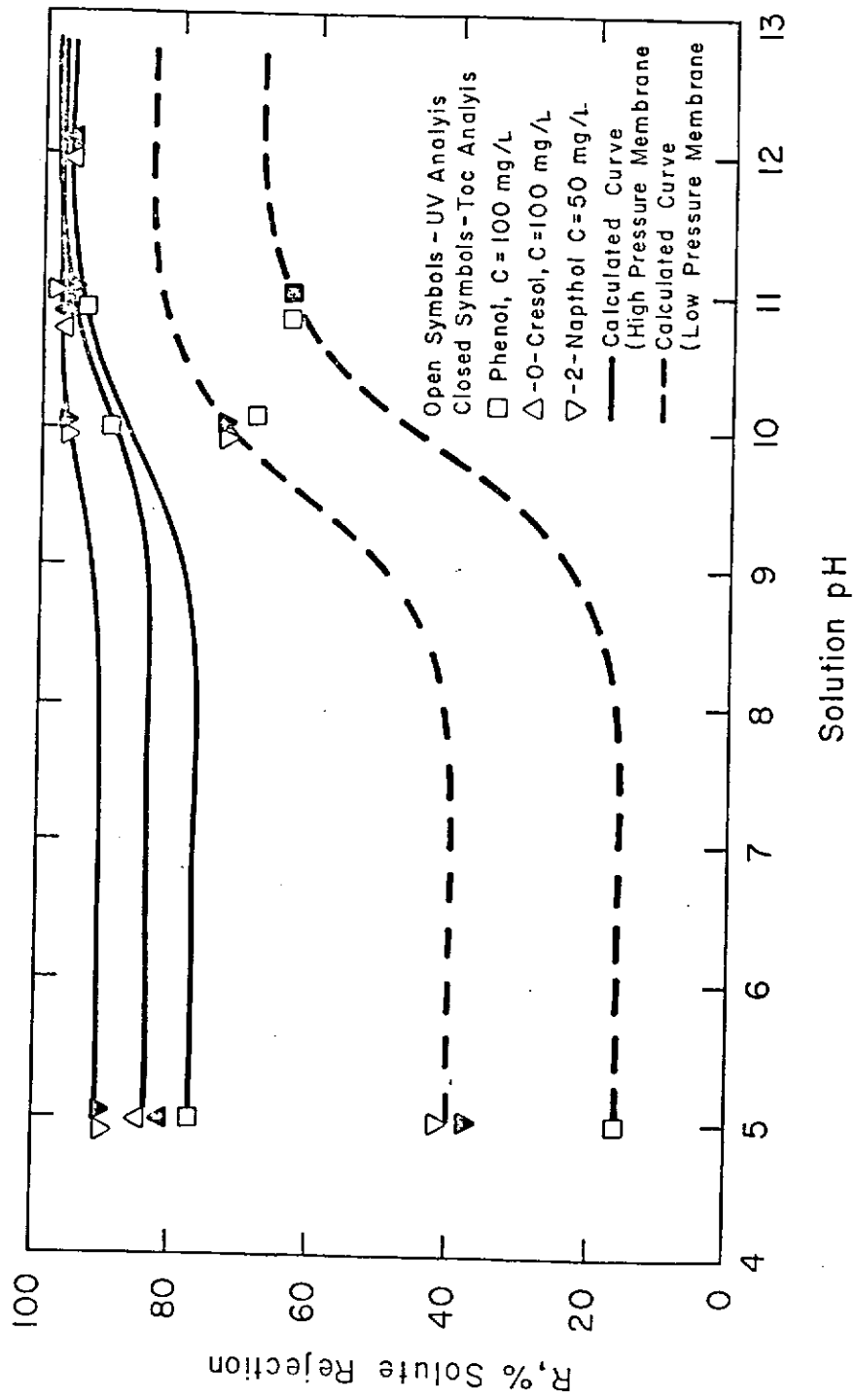


Figure 30. Membrane Separation of Phenolics as a Function of pH.

recovery, the permeate compositions were: TOC < 1.0 mg/l, Cu and Zn < 0.02 mg/l, As < 0.2 mg/l, and conductivity 75 μ mho/cm. The permeate water flux was quite high (26 gal/(ft²)(day)). Membrane operation provided waste concentration to 8x - 10x, thus resulted in significant reduction of original waste volume.

CHAPTER IV. CONCLUSIONS

The distribution coefficients were determined for B-naphthol, phenol, naphthalene and copper acetate in a water-PFD system. Naphthalene had the highest extraction value at 94, while the others had smaller distribution coefficients in the order of copper acetate, B-naphthol and phenol. Their values were 0.75 in Cu^{+2} , 0.103, and 0.040 respectively. The order of these distributions corresponded well with the degree of polarity of each compound and their solubility in water. A high degree of polarity and a high water solubility dictate a low distribution coefficient.

The distribution coefficients for B-naphthol and phenol were determined as a function of the water phase pH. The results show that the distribution coefficients for both organics increase for both low and high pH values over those obtained at neutral pH values. The hydrating properties of water was proposed as the explanation of the distribution coefficient variance.

Solubility parameters were determined for each of the solvents and solutes under investigation. The regular solution theory provided a technique to predict the distribution coefficient for each of the water-PFD-solute systems, based on the polar and nonpolar components of the solubility parameters. The predictions agreed well with the experimental values for screening purposes; they were within a factor of two. The same model was applied to other organic compounds found in coal conversion wastewaters. Predicted values of the distribution coefficients were determined for these organics based on the physical properties of the system. The applicability of these organics to the water-PFD extraction/oxidation system was deduced from the predicted values.

The extraction/oxidation of B-naphthol was affected by several parameters such as the initial pH value of the water, the water to PFD ratio, the oxidation temperature (pressure), the mixing speed, and the use of a catalyst. These parameters were adjusted to measure the change in the disappearance rate of B-naphthol, the total TOC and the intermediates.

The disappearance rates of B-naphthol and TOC increased with an initial pH value in the low or high range. This increased rate corresponded with an increase in the distribution coefficient. These results enforce the

conclusion that the oxidation reaction occurred in the PFD phase. A decrease in the water to PFD volume ratio (increase in PFD volume) increased the disappearance rate in the water of both the B-naphthol and TOC. The increased PFD volume caused more naphthol to be extracted from the water phase but it also resulted in a smaller concentration of naphthol in the PFD phase. The oxidation rate is slowed down, however, the quantity of naphthol extracted from the water phase more than compensated due to its oxidation in the PFD phase for the oxidation slow down. These results led to the conclusion that the extraction/oxidation rate mechanism is controlled by the oxidation kinetics.

The introduction of a copper catalyst into the PFD phase increased the disappearance rate of both B-naphthol and TOC. These results also led to the conclusion that the rate mechanism is determined to a large extent by the oxidation kinetics in the PFD. However, the large increase in the kinetics, as well as the discovery of a large part of the catalyst in the water phase after oxidation, indicated that oxidation also occurred to some extent in the water phase.

The disappearance rates of both B-naphthol and TOC increased with an increase in the temperature of the system. The formation of intermediates also increased with an increase in the temperature of the system. This change in intermediate formation may be linked to the relative rates of diffusion and kinetics. The effect of the water to PFD ratio demonstrated the same result as described above for the two lower temperatures, however, the reverse was true at the highest temperature. The oxidation reaction is important in both phases. At this high temperature, the shaking speed of the two phase oxidation system has a pronounced effect on the disappearance rates. An increased shaking speed increases the disappearance rate of TOC.

The formation of intermediates was dependent on the amount of B-naphthol disappearance and the reaction conditions. Generally, water phase oxidation resulted in more intermediate formation than the PFD phase oxidation for the same amount of naphthol disappearance. In the water phase, oxygen is always present in less than stoichiometric quantities. This leads to incomplete oxidation of the B-naphthol and the formation of low molecular weight organic acids and aldehydes. The PFD phase provides an excess of oxygen and leads to more complete oxidation.

Similar variables were studied for phenol extraction/oxidation. The disappearance rate of both phenol and TOC increased with an initial pH value in either the low or high range over the rate observed at a neutral pH. The distribution coefficient also increased similarly according to a change in the initial pH value, however the range of distribution coefficients is much less broad than those for B-naphthol. The effect on the disappearance rate is less pronounced for phenol with a change in the initial pH than the effect observed for B-naphthol. This link between the distribution coefficient and the disappearance rates leads to the conclusion that the oxidation of phenol occurred in the PFD phase. Thus an increased distribution coefficient causes more phenol to shift into the PFD which consequently increased the oxidation rate.

A decrease in the water to PFD ratio caused an increase in the reduction rates of both phenol and TOC suggesting a reaction controlled process. The disappearance rates of both phenol and TOC increased significantly with the addition of a copper catalyst into the PFD phase. The large increase in the disappearance rates, considering the small value of the distribution coefficient, suggested an increased oxidation rate in both phases.

An increased oxidation temperature also caused an increased disappearance rate for phenol, yet the TOC disappearance rates were not affected by the change in temperatures. Since the phenol disappearance rate is greater at the higher temperature but the TOC reduction rate is not increased, the formation of intermediates is greater at 250°C than those formed at 200°C. This increased quantity of intermediates is due to the change in the relative rates of mass transfer and oxidation. At 250°C, the oxidation of phenol in the water phase becomes appreciable. This in turn produced more intermediates due to the lack of stoichiometric oxygen in the water phase.

The oxidation of phenol in the PFD phase does not completely eliminate the formation of intermediates. The compounds formed are different than those formed during water phase oxidation. Several unidentified compounds were observed by HPLC; however, their identity was not determined. The PFD phase oxidation produced less intermediates than the water phase oxidation for a similar decrease in the phenol concentration.

Naphthalene and H-coal wastewater were also tested using this two phase oxidation technique. Naphthalene and H-coal wastewater both showed improved results over a similar one phase oxidation system. The two phase oxidation of naphthalene started with all the organic in the PFD phase. The results were similar to single PFD phase oxidation except for the diffusion of some naphthalene into the water phase before oxidation. The PFD phase oxidation of naphthalene was much faster than the water phase oxidation. H-coal wastewater demonstrated an increased disappearance rate in both TOC and some individual constituents over similar one phase oxidation runs. The availability of large quantities of oxygen in the PFD enabled the transferred organics to react at a faster rate and become more completely oxidized.

The feasibility of concentrating waste streams was also demonstrated with low pressure composite membranes. Effective separations (90%-97%) with phenolics, naphthalene, and with actual synfuel and pesticide wastes. Membrane pretreatment step prior to oxidation would result in significant reduction of two-phase reactor volume.

NOMENCLATURE

C_{AW}, C_{AW}^0	-	Concentration of organic in the water phase, initial concentration of organic in the water phase.
C_{APFD}	-	Concentration of organic in the PFD phase.
C_P, C	-	Membrane permeate and feed concentration, respectively.
COD	-	Chemical oxygen demand at any time.
COD ₀	-	Chemical oxygen demand at zero time.
K_D	-	The distribution coefficient of each organic between the two immiscible phases.
$k_L a$	-	Mass transfer coefficient.
k^1	-	Apparent first order kinetic constant.
k_p^1	-	True first order rate constant.
PFD	-	Perfluorodecalin, CIS and TRANS
R	-	Membrane rejection.
t	-	time
TOC	-	Total organic carbon of each organic in the water phase.
TOC ₀	-	Total organic carbon of each organic in the water phase at zero time.
TOCI	-	Total organic carbon due to the formation of intermediates.
α	-	Constant.

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