ABSTRACT

Wet air oxidation of dilute aqueous phenol solutions was carried out continuously in an unmixed stainless steel reactor. The range of operating conditions was--temperature: 200-250°C, pressure: 800-2200 psig, residence time: 0.25-2.0 hr, and feed concentration: 1400-3000 mg/l. Conversion of phenol was as high as 99.5%, and the main reaction products were determined by analysis to be carbon dioxide and water, along with a small amount of carbon monoxide (about 300 ppm). At 200°C there was a tendency for the phenol to form tars which collected in the flow system and discoloured the effluent. At 250°C the tar formation was minimal and caused no problems. At pressures below 1200 psig the oxidation reaction was found to be controlled more by mass transfer than by chemical reaction, while at higher pressures the reverse was true. The wet air oxidation process is promising as a means of pollution control because it is relatively insensitive to changes in feed concentration and flow rate.

ACKNOWLEDGEMENT

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Thanks are also extended to Mr. G. Gasperetti and his Machine Shop Staff for their assistance in assembling the pilot plant.

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NOMENCLATURE

a	interfacial area, cm^2/cm^3
b	intercepts of curves in Figures 9 and 10
c	liquid concentration, g-mole/l
c*	equilibrium oxygen concentration in liquid, g-mole/l
c_L	oxygen concentration at the reaction site, g-mole/l
D	diffusivity, cm^2/sec
E	activation energy, cal/g-mole
H	Henry's Law constant, (l-atm)/g-mole
k	mass transfer coefficient, cm/sec
k_R	chemical rate constant
k_{Ro}	Arrhenius' equation constant
m	slopes of curves in Figures 9 and 10
n	number of moles
m',n'	exponents in chemical rate equation
p	partial pressure, psia
P	total air pressure, atm
r	reaction rate, g-mole/(l-hr)
R	gas law constant, (l-atm)/g-mole - ^oK
T	temperature, ^oC or ^oK
V	reactor volume, l
Re	Reynolds number, dimensionless
Sc	Schmidt number, dimensionless

ρ	liquid density, g/cm^3
τ	reactor residence time, hr
μ	liquid viscosity, cp

INTRODUCTION

In recent years the pollution of our environment by wastes of all types has become quite widespread, and the general public has become more aware of the problem because pollution now affects a large percentage of the world's population. Increasing concern over the effects of environmental pollution has led to legislation which sets acceptable limits on discharges from such sources as chemical plants, power generating stations, automobiles, and manufacturers of all sorts. Some pollution problems are relatively easy to solve. For example, the installation of an electrostatic precipitator on an exhaust stack will almost completely remove solid particles from the gas. On the other hand, many pollution problems such as the removal of dissolved organics from waste waters require a considerable amount of research and study before effective and economical solutions are found.

Phenol is a typical organic water pollutant which can be found in the effluent streams of oil refineries, petrochemical plants, and steel mills. Phenol is toxic in higher concentrations and, like many organic chemicals, it will create an oxygen demand upon the body of water into which it is discharged, thereby upsetting natural environmental processes. When phenol-containing waters are processed by municipal water treatment plants the phenol is converted to chlorinated phenols which are

detectable by taste in the 5 ppb range[1]. For these reasons it is desirable to limit the discharges of phenol and other offensive chemicals, and certain government agencies have taken steps to acieve this[2].

Several methods such as biological oxidation, solvent extraction, oxidation with ozone, and adsorption are currently being used to treat waste streams containing small amounts of organics[3]. Of these, biological oxidation, which involves the destruction of organic matter by living organisms, is the most widely used. These processes are effective in reducing the chemical oxygen demand of waste streams, but they must be designed for fairly definite feed concentrations; since the composition of a given waste stream can vary considerably from day to day the outlet concentration of pollutants from the treatment facility may also fluctuate to a considerable extent. A process which could handle a wide variety of organic pollutants in varying concentrations and produce a fairly constant effluent concentration would provide an attractive alternative as a means of pollution control.

Many organic compounds will be oxidized readily when combined with air at elevated temperatures and pressures. An industrial process based on this fact has been developed[4] and shown to be successful in treating waste streams such as pulp mill effluents and municipal sewage.

The basis for this thesis is to use this high temperature and pressure oxidation process to study the

removal of phenol from dilute aqueous solutions and to gather some basic kinetic information about the oxidation reaction.

LITERATURE SURVEY

1. Process Background

The process being considered in this work is the wet air oxidation process, so called because it oxidizes organic substances which are dissolved or suspended in water, using compressed air. The process was first developed as a continuous operation in the mid-1940's in the United States by Zimmermann[4] and is usually referred to as the "Zimmermann process". The basic idea behind the process is to combine a waste stream and air under suitable conditions (typically 200-250°C and 1500-2500 psig), and under these conditions the unwanted waste material will be almost completely converted to carbon dioxide, water and ash (if the waste is a solid). The key to the process is that there must always be some liquid water present for the reaction to proceed.

Zimmermann developed the process as a means of disposing of industrial wastes[5]. He found that the Chemical Oxygen Demand (C.O.D.) of streams such as pulp mill effluents, sewage wastes, dairy wastes, and oil refinery wastes could be reduced by 80-90%, and as long as the reactor temperature was 250°C or higher, the C.O.D. of the treated stream was low and relatively independent of the C.O.D. of the feed stream. He also found that it was not necessary to supply excess air to the reactor. The percentage of C.O.D. removed increased sharply at temperatures of 225°C or higher and the principal conclusion

was that this range of temperature was best for maximum C.O.D. removal.

Zimmermann's reactor was designed so that most of the volume was occupied by air and steam, with only a minor percentage occupied by liquid. In his early studies the pressure and temperature were always varied together and so it could not be determined if they had independent effects on the reaction. Presumably he chose to vary both together so that he could keep a constant liquid-to-gas ratio in the reactor.

A later Zimmermann paper[6] discusses more details of the process. In studying the temperature effect Zimmermann found that between 250°C and 330°C a rise of 15 degrees in reactor temperature permitted at least twice the volume of feed liquor to be oxidized in the same time. Again, though, it was necessary to raise the reactor pressure when the temperature was increased, to maintain some water in the liquid phase. Some runs were done at a constant temperature and different pressures. At 275°C the reduction in C.O.D. obtained at 1500 psig(79%) was about the same as at 1200 psig even though the flow rate had been increased, while the percentage removal at 1800 psig(85%) was higher than at 1200 psig even after the flow rate had been doubled. This effect of pressure showed that the residence time in the reactor could be decreased if higher pressures were used, thereby making the processing equipment more compact.

Proof that the process provided complete oxidation

using stoichiometric quantities of oxygen was given by the results of Zimmermann's runs in which he used slurries of carbon and sulfur as feeds. In each case only CO_2 and SO_3 were found in the exit gases and no CO or SO_2 was detectable.

Under some conditions with waste streams as feed varying amounts of volatile organics such as acetic acid were found. These did not undergo further oxidation in the reactor, but were oxidized when passed through a catalytic converter.

Zimmermann stressed the potential industrial applicability of his process in these and other papers[7,8]. It is interesting to note that, in addition to being a means of pollution control, the Zimmermann process can also be used in certain industrial situations to produce steam and/or electrical energy, thus making itself energetically self-sufficient. This is a key factor when the Zimmermann process is being considered because it can improve the often negative aspects of pollution control economics.

2. Application to Phenol Oxidation

The first application of the wet air oxidation process to the oxidation of phenol in waste water was by Shmidt[9]. He used a batch-type, agitated reactor and studied the reaction under a wide range of operating conditions; temperatures ranged from 150°C to 300°C, pressures from 1075 psig to 2275 psig, contact times from

30 minutes to 2 hours, and feed concentrations from 10,000 mg/l to 50,000 mg/l. Shmidt's results closely parallel those of Zimmermann because they show a considerable increase in the conversion of phenol between 150°C and 225°C, but above that the increase is small for further temperature increases. Shmidt did not study the effects of different pressures at a fixed temperature, or vice versa. His results are very good as he achieved phenol conversions as high as 99.99% with final concentrations as low as 2.5 mg/l. Purification with respect to C.O.D. was as high as 98.4%.

Shmidt's analysis showed that the end products of the reaction were carbon monoxide, carbon dioxide, and acetic and formic acids. The formation of CO seems to indicate that not enough oxygen was supplied because previously Zimmermann had found no indication of CO production when just stoichiometric amounts of oxygen were used. Shmidt stated that 30-50% excess oxygen was always supplied but calculations can be done which indicate that this may not always have been so (see Appendix).

Shmidt found that at temperatures in the 150°C to 200°C range the liquid product was dark-coloured but he did not state what caused this discoloration. At higher temperatures (up to 300°C) the purified water was colorless. Shmidt made some runs using an acetic acid solution as feed to determine if it would be oxidized readily and he found that it had a high resistance to oxidation. Thus if the

reaction conditions are such that a considerable amount of the phenol is converted to acetic acid, the acid will not be oxidized to any appreciable extent in this type of reactor and further treatment of the waste stream would be necessary. This finding agrees with Zimmermann's results.

Stepanyan et al[10] have followed the work of Shmidt by studying the liquid-phase oxidation of phenol, methanol, and formaldehyde, again in a batch reactor. They considered various mixtures of the three organics as well as solutions of each one, but they used only one set of operating conditions: 200°C, 600 psig, and a residence time of 90 minutes. They achieved a 94.7% reduction in C.O.D. for the phenol-water solution which had an initial concentration of 25,000 mg/l. No detailed studies of the various oxidation reactions were made, but they did show that aqueous solutions of more than one organic compound can be oxidized successfully to a considerable extent: the percentage reduction in C.O.D. for a solution of phenol, methanol, and formaldehyde in water was 80%. This fact increases the potential applicability of the wet air oxidation process because any given waste stream would be certain to contain more than one pollutant.

A modification of the Zimmermann process has been patented by Pope[11], but he uses a catalyst (usually a combination of metal oxides) in addition to elevated temperatures and pressures to achieve the oxidation. The catalytic process can be used on a wide variety of organics

and is especially good for those such as acetic acid which are not readily oxidized by the Zimmermann process. A catalytic reactor would likely be of most use if it were installed following a wet air oxidation reactor as the latter would convert most of the pollutants to harmless products and the former could then remove the small amounts of pollutants remaining.

3. Solubility and Diffusivity Data

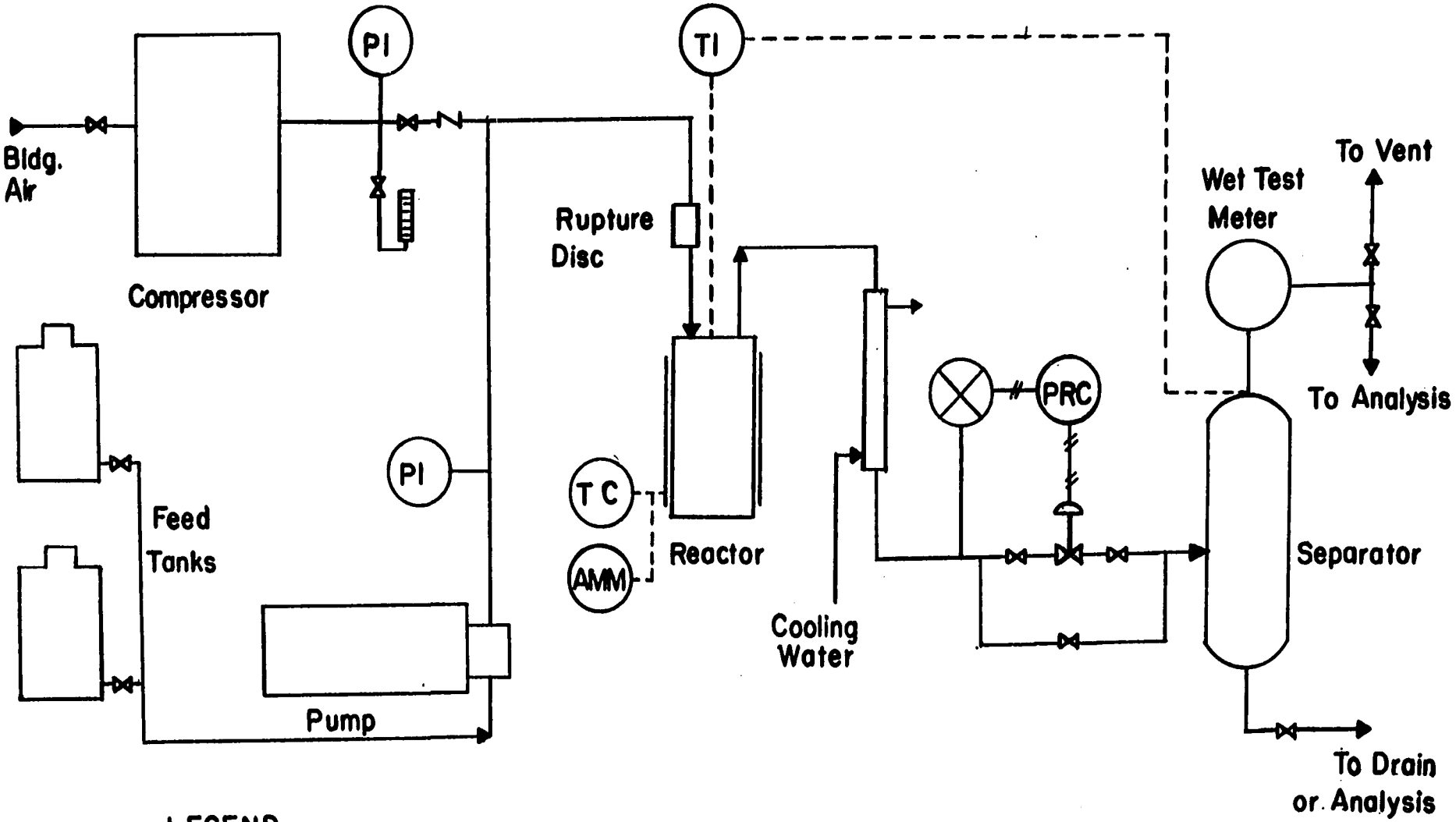
There are some data available in the literature on air-water systems. Himmelblau[12] has collected a vast amount of data on the solubilities of inert gases in water and he gives data on specific gases as well as a generalized solubility correlation. The data are in the form of graphs of Henry's Law constant vs. reciprocal absolute temperature. It is interesting to note the shape of these curves: all are concave downward which means that there is a maximum value of H for each gas, and this represents the minimum solubility. For example, oxygen has its minimum H at 97°C, but values of H at both 10°C and 200°C are the same. This indicates that we can expect a reasonable degree of oxygen solubility in water under operating conditions which are typical of the wet air oxidation process.

St.-Denis and Fell[13] have correlated the diffusivity of oxygen in water up to 60°C from a large number of sources. These data are useful when mass transfer effects are being studied, instead of relying on generalized prediction methods. However, since the wet air oxidation

process usually operates at temperatures in excess of 200°C the usefulness of these diffusivity data is somewhat limited in this application.

4. Basis for This Thesis

The work and results discussed above show that the wet air oxidation process has been operated successfully on a commercial scale and that it is promising as a pollution control measure for the treatment of dissolved combustible organics in water. The results obtained in the batch-wise oxidation of phenol solutions are very good and they justify the application of the process in a continuous system. The aim of this thesis is thus to construct and operate such a system, and to gather data which will be useful in studying the oxidation reaction.



LEGEND

PI	Pressure Indicator	TI	Temperature Indicator
PRC	Pressure Recorder/ Controller	TC	Temperature Controller
⊗	Pressure Transmitter	AMM	Ammeter

Figure 1. Sketch of Experimental Apparatus

EXPERIMENTAL

1. Apparatus

The apparatus used in this work is actually a small-scale pilot plant. The design of the pilot plant was based on sketches in Zimmermann's papers, with some modifications to suit the scale of operation. The principal alteration was the deletion of several heat exchangers which Zimmermann used for feed preheating. Figure 1 is a diagrammatic flowsheet of the pilot plant.

Two feed tanks were used - one for distilled water and one for the phenol solutions. The reason for this is discussed below under "Procedure". Each feed tank is a 13-gallon polyethylene bottle with spigot, number B7586-13, supplied by Canadian Laboratory Supplies Limited.

All pressure tubing, valves, and fittings are ¼" LP (low pressure) 316 stainless steel, supplied by Pressure Products Industries, Hatboro, Pennsylvania.

The air compressor is a reciprocating , diaphragm-type, two-stage machine, model Q-071038, supplied by Pressure Products Industries. Maximum throughput is 125 scfh at 5000 psig discharge pressure. The compressor output is regulated by a needle valve and a rotameter in the discharge line. The rotameter is a Brooks, tube size R-6-15-B, with a stainless steel float.

The pump is also a diaphragm-type positive displacement machine, model CP-3 "Pulsafeeder", supplied by

Interpace Corporation, Lapp Insulator Division, Le Roy, New York. Pump capacity ranges from 242 USgal/hr at 50 psig to 0.85 USgal/hr at 5000 psig. Output is regulated by adjusting the piston stroke-length.

The compressor and pump both have identical discharge pressure gauges connected to them. They are the model W-5-1 "Astragauge", supplied by Pressure Products Industries.

The reactor is a stainless steel cylinder of 1 litre capacity. All connections are in the cover, which screws into the body. There is an inlet connection equipped with a dip tube, an outlet connection, and a thermocouple connection. The reactor was made to order by Pressure Products Industries.

The heat exchanger was manufactured in the Department Machine Shop. It contains one tube, which is a piece of LP stainless tubing, and the shell is 1½" I.D. copper pipe. Cold water in the shell runs counter-current to the process stream.

The gas/liquid separator was obtained from the Department's spare parts supply room. It is made of stainless steel, and is 23" high by 8" O.D. A thermocouple was installed to record the liquid temperature in the bottom of the separator.

The reactor is heated by ten electrical strip heaters connected in series. They are model SE-1202, 250 watts each, supplied by Canadian Chromalox Limited, Toronto.

The reactor is insulated with a 1" layer of asbestos cement, and wrapped in eight layers of asbestos paper.

The reactor heater temperature controller is a Brown Pyr-O-Vane, range 0-1400°F, supplied by Honeywell Controls Limited.

The pressure control system is a standard three-part system supplied by Honeywell Controls Limited. The pressure transmitter is a non-indicating type, model 738 N1H3, range 0-4000 psig. The pressure recorder is a model 51311 with an integrally mounted two-mode controller, model 52201. The control valve is a $\frac{1}{4}$" Research Control Valve, supplied with various trims.

The temperature indicator/recorder is an Electronik 16 Multi-point Strip Chart Recorder, supplied by Honeywell Controls Limited. It will record up to 12 temperatures and has a range of 0-400°C.

The wet test meter is a "Precision" type, number 11-166-5, capacity $\frac{1}{10}$ cubic foot, supplied by Fisher Scientific Co., Limited.

A hand pump was used for dead-weight pressure testing of the system before it was operated. The pump was supplied by Pressure Products Industries, and is model OH-100-15.

The phenol was purchased in crystal form from Canadian Laboratory Supplies Limited. It was "Baker Analyzed Reagent" grade. Distilled water was used in the preparation of all feed solutions.

The air fed to the suction of the compressor was taken from building supply air lines, and was filtered and dried to ensure its cleanliness.

2. Assembly and Calibration of Equipment

Once an equipment layout had been decided upon the actual assembly was done mainly by the Machine Shop staff because of their familiarity with pressure fittings and equipment. The system was pressure-tested to check for any leaks. This was done with the hand pump mentioned above at a pressure of just under 5000 psig. This pressure was chosen because the rupture disc in the reactor feed line will burst at just over 5000 psig.

The compressor calibration data had been supplied, as had the rotameter data, so flow rates there were known. The pump was calibrated at various discharge pressures. All instruments except the temperature controller were new and needed no calibration as they had been calibrated before being shipped. As a check that the pressure gauge calibration had not changed, the compressor was run by itself and both pressure gauges showed identical discharge pressures. It was decided that calibration of the temperature controller was not important because the thermocouple inside the reactor would give the temperature there.

Soon after the pilot plant was first started up it became apparent that the compressor was too noisy and that some measures would have to be taken to remedy the situation.

Several alternative solutions to the problem were considered, and it was decided to construct a plywood box around the compressor, and to line it with fibreglass insulation. Suitable access doors were provided, and it was also necessary to install a fan in one wall of the box to provide adequate cooling for the compressor.

3. Procedure

The operating procedure for a typical run was as follows (note that the heaters were left on at all times to minimize any heating-cooling strain on the reactor):
(i) a phenol solution of the desired concentration was prepared and a sample was taken;
(ii) the desired pump setting was selected and the pump was started using distilled water as feed. Distilled water was used to prevent the build-up of tar deposits in the reactor, which would occur because the reactor was hot and the first water entering the reactor was vaporized;
(iii) when the reactor was full of water and the desired operating pressure had been reached the pressure controller was switched to "automatic";
(iv) while the reactor was filling with water the compressor was isolated and started, and all of its output was discharged through the bleed rotameter;
(v) when step (iii) had been completed the compressor discharge valve was opened and the bleed valve was adjusted to give the desired net output;
(vi) when the desired temperature and pressure were reached

the phenol solution feed was started;

(vii) after five residence times liquid and gas samples were taken. This was repeated for one or two residence times thereafter;

(viii) the feed was switched back to distilled water so that all of the phenol solution in the reactor would be pumped out before the pump and compressor were shut down.

4. Analysis

Two methods are available for analyzing for phenol in water, both of which are found in the ASTM Standards[14]. Method D1783-70 is a wet method involving distillation of the sample and a colorimetric analysis on a spectrophotometer. This method is suitable for very low phenol concentrations, but because it is time-consuming, its use is only justified when the phenol concentration in the sample is below 1 ppm, the lower limit of detection for the other method.

The second method, D2580-68, uses gas-liquid chromatography. It is much simpler to use and is just as accurate once a reproducible injection technique has been mastered. The column was calibrated with solutions of known concentration and from this work a "standardization value" was computed which was used in the calculations for actual samples. The interpretation of the chromatograms was done using the "cut and weigh" method. The details of these calculations are given in the Appendix.

The chromatograph used for phenol analysis was a

Varian Aerograph model 1400 with a flame ionization detector connected to a Honeywell Electronik 194 Lab Recorder. The chromatographic column was a $\frac{1}{8}$" by 5' stainless steel column packed with 60/80 mesh Chromosorb W (acid washed) coated with 5% by weight Free Fatty Acid Phase.

The C.O.D. determination was done using the dichromate method, taken from Standard Methods[15]. The sample was refluxed with a mixture of chromic and sulfuric acids and then the excess dichromate was titrated with ferrous ammonium sulfate.

The gas analysis was also done by chromatography because the concentration of carbon dioxide in the effluent gas was too low to be detected by a method such as the Orsat method. A two-column analysis method was used, with column temperatures of 30°C and injector and detector temperatures of 60°C. The columns were calibrated using a calibration gas containing 1.06% carbon dioxide in air, purchased from Matheson of Canada Limited. Chromatogram interpretation was again by the "cut and weigh" method, and details of these calculations may be found in the Appendix.

The chromatograph used for gas analysis was a Varian Aerograph model 1420 with a thermal conductivity detector. A Varian recorder, model A-25, was used in conjunction with the chromatograph. Two columns were used: one was a $\frac{1}{8}$" by 6' stainless steel column packed

with 80/100 mesh Porapak T, the other was a $\frac{1}{8}$" by 6' stainless steel column packed with 80/100 mesh Molecular Sieve 13X.

5. Theoretical Basis for Experimental Runs

The overall experimental objective for this project is to study the oxidation of phenol in dilute aqueous solutions at elevated temperatures and pressures and, if possible, to get an indication of what factors are important in the reaction control mechanism.

The first few experimental runs were made to ensure that the pilot plant would operate smoothly and that the oxidation of phenol could be carried out successfully. During these initial runs the air flow rate was 1.2 times the stoichiometric requirement. It was felt that a constant air rate (at conditions) would eliminate one variable in studying the reaction so a rate of 0.5 ft^3/hr at conditions was chosen for subsequent runs. This choice was based on two things: (i) a bubbling experiment in a glass cylinder showed that this flow rate provided good agitation in the liquid, and (ii) the operating characteristics of the pilot plant indicated that this rate was comfortably within the capacity range of the equipment. Once the "breaking in" period had been completed a systematic study of the effects of temperature, pressure, feed concentration, and residence time on the reaction was made.

If the reaction rate is controlled only by mass transfer of oxygen to the reaction site (i.e. if the

chemical reaction is very fast) then the rate expression will be of the form

$$\text{rate} = k\,a\,(c^* - c_L).$$

Since it has been assumed that the chemical reaction is very fast, all oxygen reaching the reaction site will be consumed immediately, so that $c_L = 0$. The rate expression then becomes

$$\text{rate} = k\,a\,c^*.$$

The interfacial area a will be constant because the gas volume in the reactor will be constant. The only remaining variable is c*. From Henry's Law we know that

$$p_{O_2} = H\,c^*.$$

The rate expression then becomes

$$\text{rate} = (ka)\,c^* = \left(\frac{ka}{H}\right) p_{O_2}.$$

Thus if mass transfer is the only factor affecting the overall reaction rate,

$$\text{rate} \propto p_{O_2}.$$

If the chemical reaction rate expression is of the form

$$r = k_R\, c_{O_2}^{m'}\, c_{\text{phenol}}^{n'}$$

it follows that the chemical rate could be simplified to

$$r = k_R \left(\frac{1}{H}\right)^{m'} p_{O_2}^{m'}\, c_{\text{phenol}}^{n'}$$

and again the rate would be affected by the partial pressure of oxygen. Of the two rate constants, $k_R/H^{m'}$ would be the more temperature-sensitive inasmuch as

$$k_R = k_{Ro} \exp(-E/RT)$$

and

$$k \propto D\,(Re)^{0.5}\,(Sc)^{0.33}, \text{ for turbulent flow}^{16}.$$

Maintaining the pressure and increasing the temperature should thus have a large effect on the overall reaction rate if it is chemical reaction controlled, and a smaller effect otherwise.

There is an additional complication having to do with where the reaction actually occurs: either at the gas/liquid interface, or in the liquid film around the gas bubbles, or in the bulk liquid. This depends on a number of factors such as the speed of the reaction (instantaneous, fast, or slow), the concentrations of the reactants, and the solubility of the gas in the liquid[17]. Determination of the location of the reaction zone is quite complex, involving parameters such as the diffusivities of oxygen and phenol at high temperatures and the mass transfer coefficients of oxygen in both gas and liquid phases. The study of this aspect of the phenol oxidation reaction is a long-term research goal but is beyond the scope of this thesis.

The above analysis was used as a basis for the experimental runs. It was decided to do several sets of runs studying two temperatures, four pressures, two feed concentrations, and several liquid flow rates. The details of the runs are tabulated in the Appendix.

RESULTS AND DISCUSSION

The experimental data were all collected when the pilot plant was operating under steady state conditions. The time taken to reach steady state was determined experimentally in early runs and the result was that after approximately five "residence times" the system could be considered to be at steady state. This corresponds to approximately a 99% exchange of the contents for a step change in the feed to a continuous stirred tank reactor[18]. The residence time for the reactor was considered as being the liquid holdup time, i.e. very little volume was occupied by gas. This was based on a bubbling experiment in an open cylinder having the same dimensions as the reactor. When air was bubbled through water at the same volumetric rates which were used in the experimental runs the total fluid volume was increased by less than 0.5%; hence the definition of residence time.

The first ten experimental runs, which are summarized in Table 2 in the Appendix, gave early indications that the wet air oxidation process would effectively remove phenol from dilute aqueous solutions, but they also indicated a major problem. Under some operating conditions (around 200°C and 1000 psig) phenol appears to react with oxygen to form phenol tars, which are dark brown and quite viscous. Early runs in which no oxygen was present did not form tars. The tars are believed to be phenolic polymers, and are very soluble

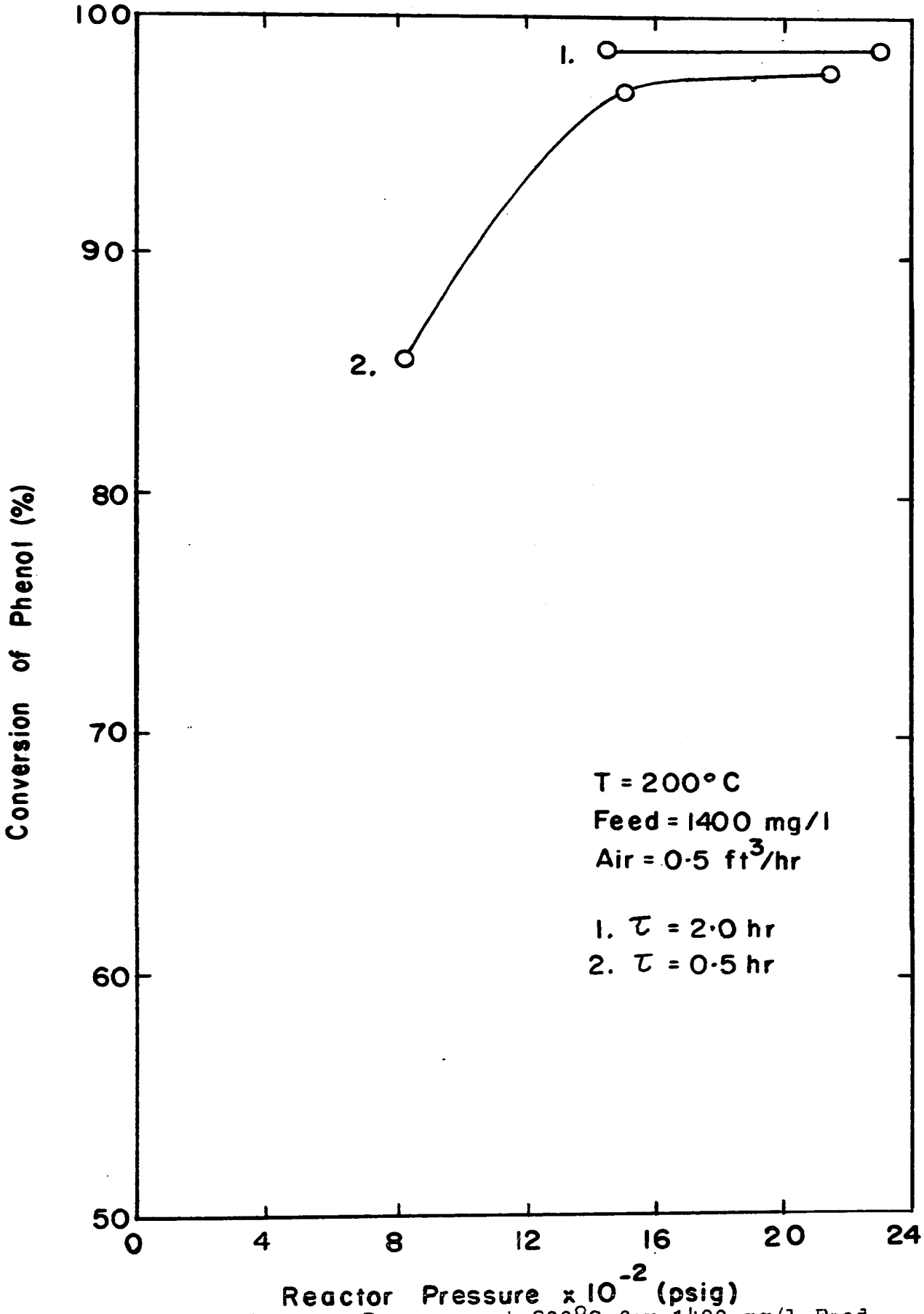


Figure 2. Conversion vs. Pressure at 200°C for 1400 mg/l Feed

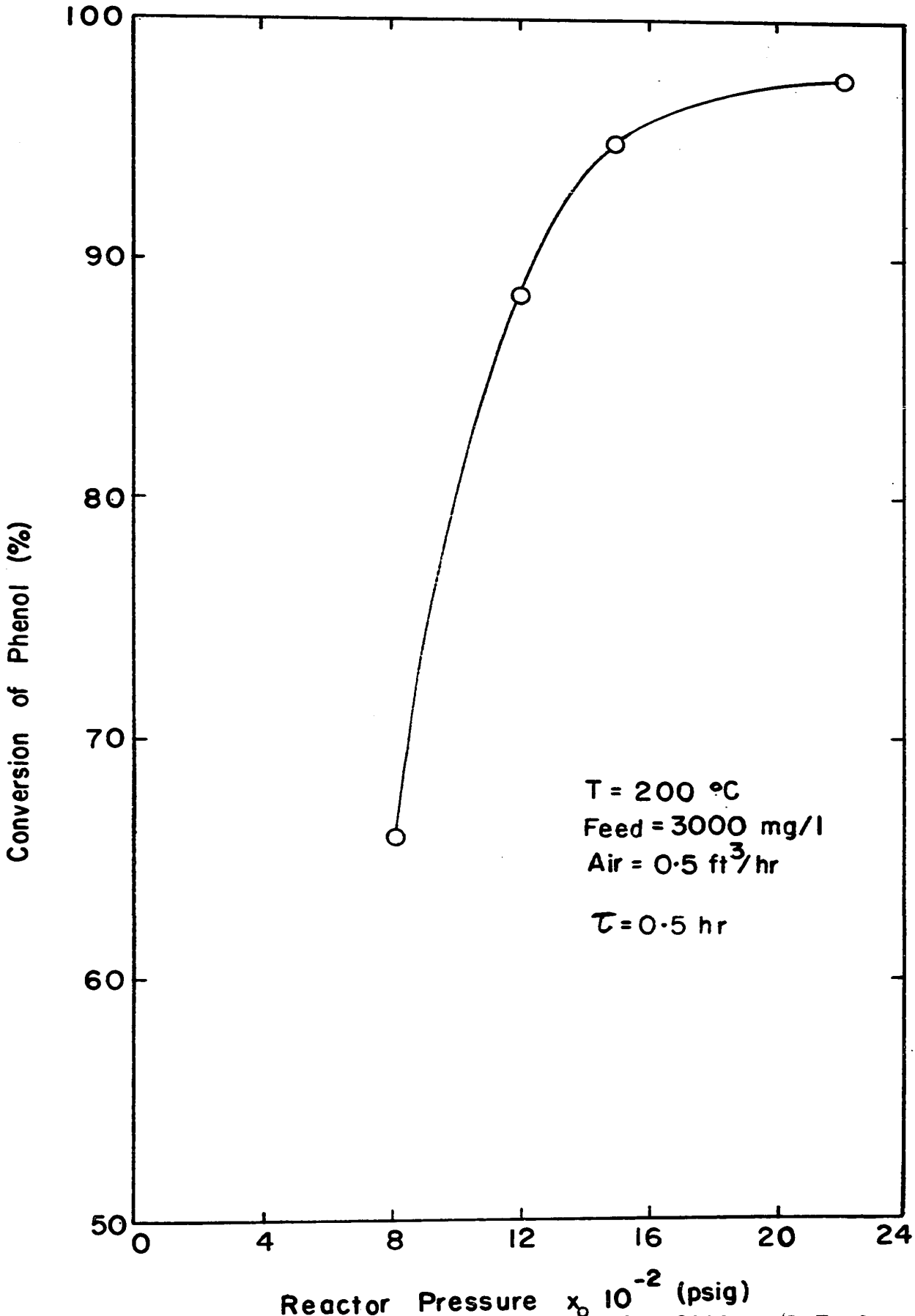


Figure 3. Conversion vs. Pressure at 200°C for 3000 mg/l Feed

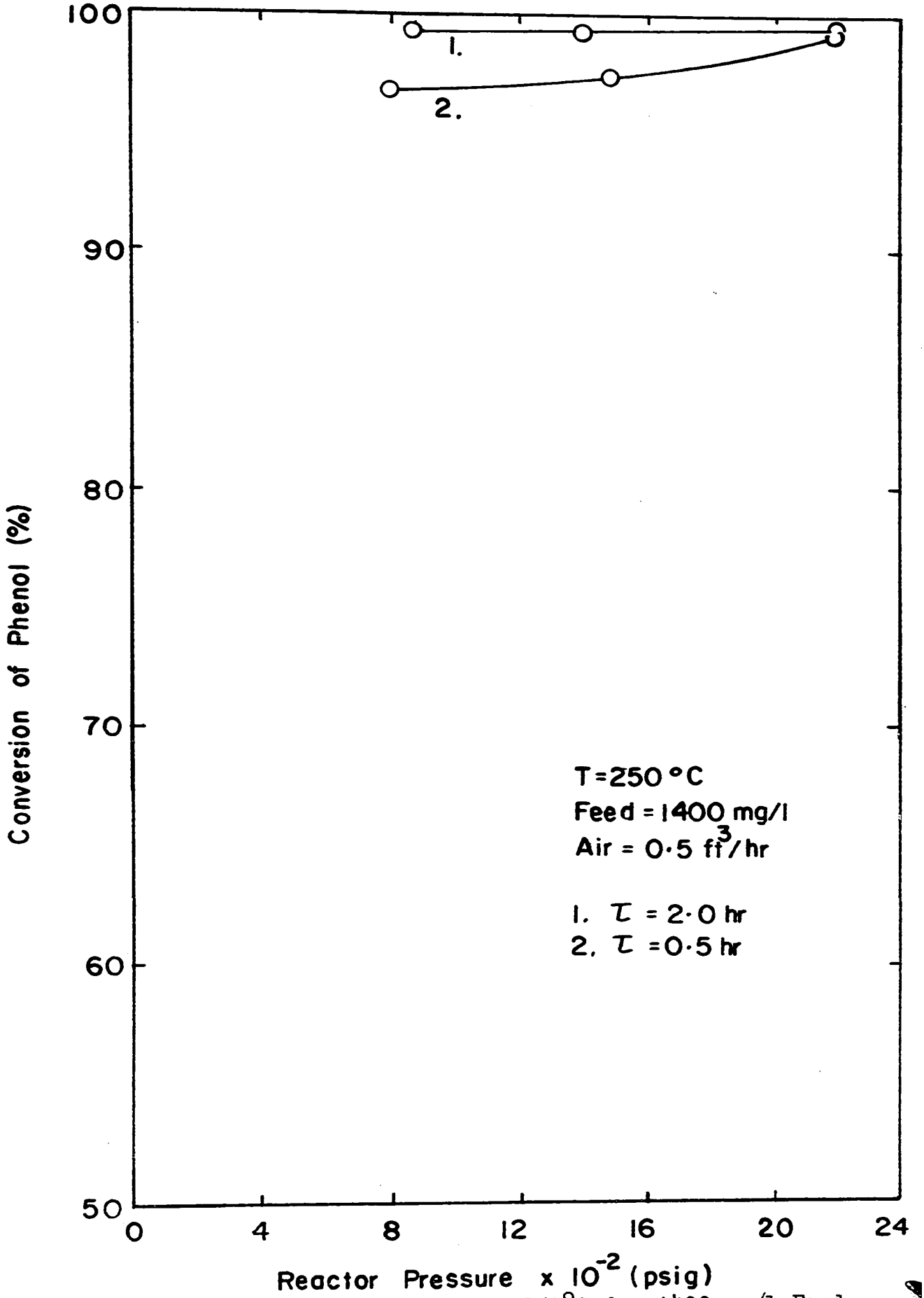


Figure 4. Conversion vs. Pressure at 250°C for 1400 mg/l Feed

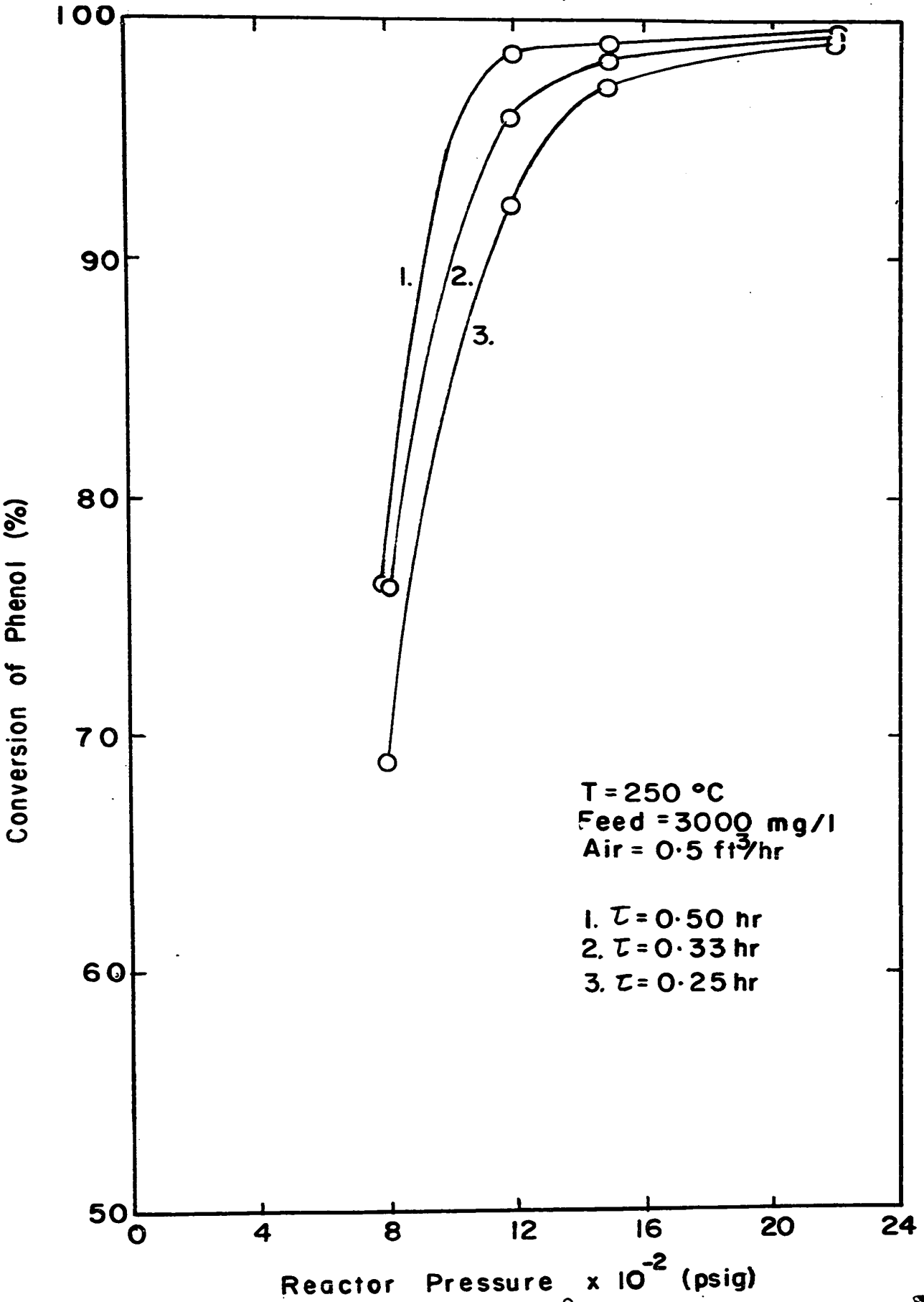


Figure 5. Conversion vs. Pressure at 250°C for 3000 mg/l Feed

in methanol, but are only slightly soluble in water at room temperature. When the tars were produced they accumulated in and near the control valve and completely plugged it on some occasions. Since the disassembly and cleanout of the system is a tedious procedure every effort was made to avoid using operating conditions which would necessitate unscheduled shut-downs. The only runs which caused serious difficulties were those in which a relatively high feed concentration (34,000 mg/l phenol) was used. These runs were undertaken in an attempt to duplicate the results of Shmidt[9] but were abandoned because of the tar problem. In Shmidt's batch reactor the tars would not cause serious problems because they would just accumulate in the reactor. The plugging problem which caused shut-downs of the continuous reaction system would not be encountered. For all subsequent runs the phenol feed concentration was in the 1000-3000 mg/l range because this is the range which seems to be more typical of plant waste streams[3].

The experimental results are given in the Appendix. Figures 2 to 8 are based on these tabulations.

Figures 2 and 3 show the change in phenol conversion with reactor pressure for several runs at 200°C. Figures 4 and 5 are the equivalent curves at 250°C. As can be seen in the figures the percentage of phenol reacted is usually quite high, especially at the higher temperature. The results at 250°C are more interesting because the tar

formation is considerably less and hence a practical application of the wet air oxidation process would be more likely to operate at the higher temperature. Figure 4 shows that, with a feed concentration of 1400 mg/l, conversion is very high and quite constant over a considerable range of pressures. Since conversion is almost constant, so is the reaction rate, and under these conditions the reaction seems to be chemical reaction controlled, i.e. the rate is limited by the low phenol concentration in the reactor.

The same thing is true of the higher pressure range of Figure 5, but at lower pressures the conversion of phenol is markedly less. Table 1 compares the reaction rates at pressures of 800 psig and 1200 psig. From the table it can be seen that the increase in reaction rate is approximately half the increase in oxygen partial pressure for the three cases considered. It was postulated previously that if the reaction was controlled solely by mass transfer the overall reaction rate would vary directly with partial pressure, i.e. the ratio of the rates at two different operating pressures would equal the ratio of the corresponding oxygen partial pressures. Since it has been shown that this is not so it is apparent that the overall reaction control mechanism is complex and that it changes at different operating pressures. In the lower pressure region of Figure 5 mass transfer seems important because the rate depends to some extent on the oxygen partial pressure,

TABLE 1

COMPARISON OF REACTION RATES AT DIFFERENT PRESSURES

Data are taken from Figure 5 and Tables 3, 4, and 6.

Reaction rates are in g-mole/(l-hr).

		Total Pressure (psig)		
		800	1200	r_{1200}/r_{800}
Residence Time (hr)	0.50	0.04960	0.06406	1.292
	0.33	0.07413	0.09344	1.260
	0.25	0.08918	0.12004	1.346

Partial pressure of oxygen at 250°C, 800 psig = 50 psia

Partial pressure of oxygen at 250°C, 1200 psig = 134 psia

Ratio of partial pressures = 2.680

Therefore,

$$(r_{1200}/r_{800}) \approx 0.5\ (p_{1200}/p_{800}).$$

but the relatively low phenol concentration also influences the reaction rate, so that the control mechanism in that region is a combination of mass transfer and chemical reaction control. The higher pressure region, as was mentioned previously, seems to be under chemical reaction control.

A further indication that mass transfer is important at pressures below 1200 psig is given by Figures 6 and 7. These figures compare the results from Figure 5 with the results of runs in which the air flow rate to the reactor was doubled, to 1.0 ft^3/hr at conditions. Since the previous air rate had already provided considerable excess air (see Appendix), the additional flow served only to increase the degree of turbulence in the reactor. The figures show that higher conversions were obtained in the lower pressure range. Since an increase in agitation will usually promote better mass transfer by making more bubble surface area available for mass transfer, the higher conversions found with the higher air rate indicate that resistance to mass transfer was lowered.

The effect on reaction rate of increasing the temperature while holding the pressure constant can be seen in the results of runs 23 to 28, from Table 3 (Appendix). At 800 psig, raising the temperature from 200°C to 250°C increased the rate by 13.8%. Similarly at 1500 psig and 2200 psig the increases were 14.8% and 16.7% respectively. This shows that the reaction is

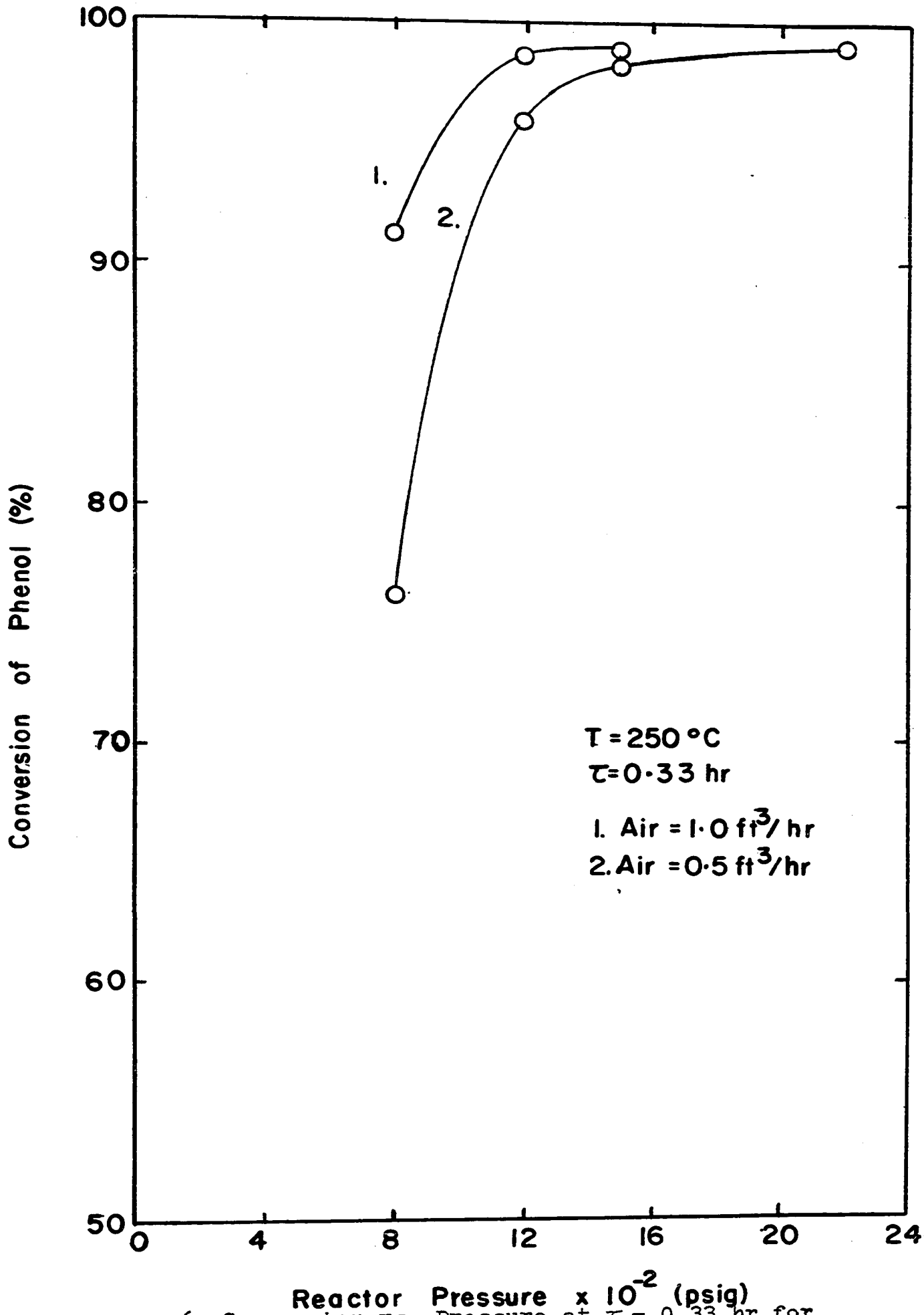


Figure 6. Conversion vs. Pressure at τ = 0.33 hr for Different Air Rates

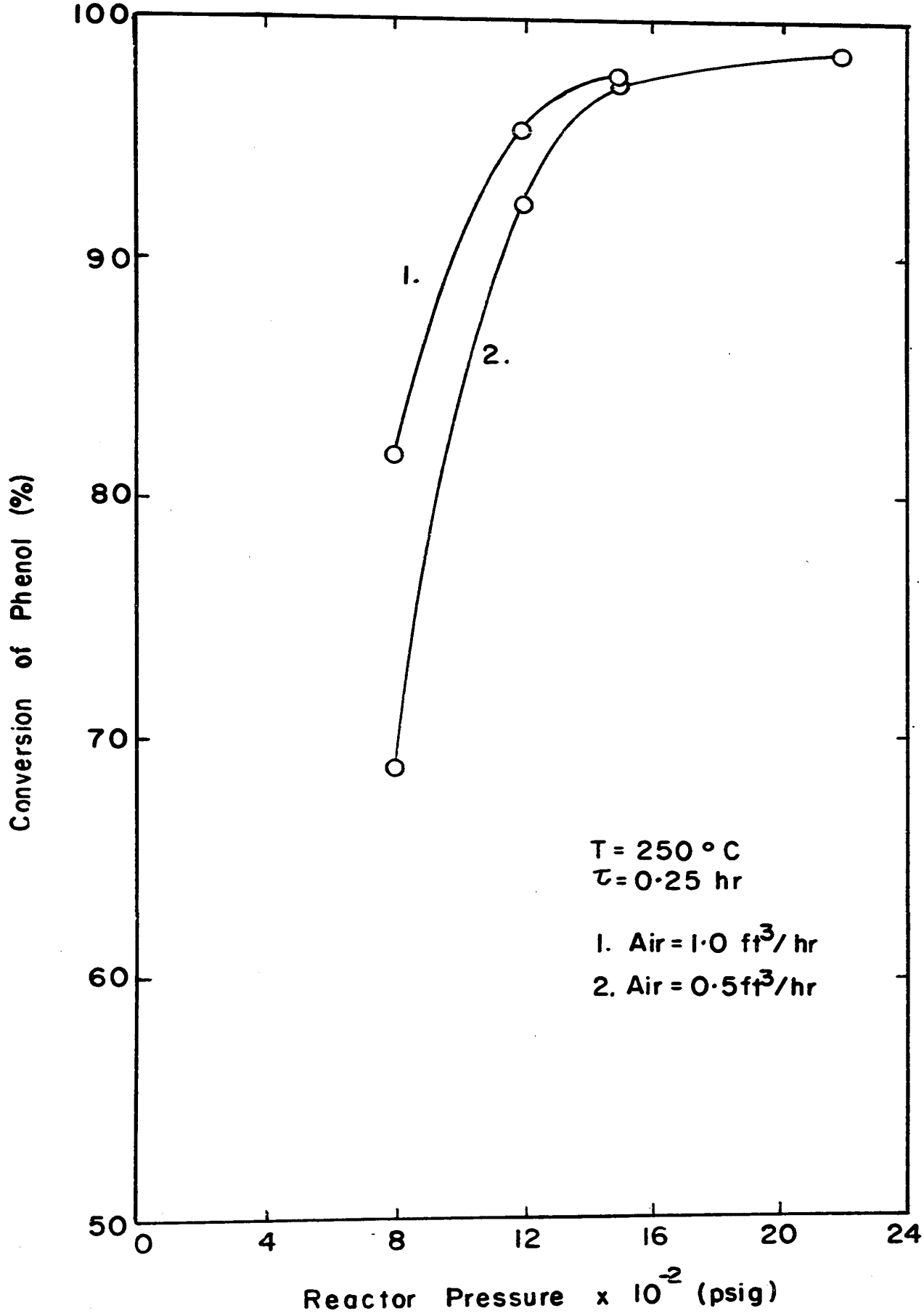


Figure 7. Conversion vs. Pressure at τ = 0.25 hr for Different Air Rates

partly chemical reaction controlled in all pressure regions and to an increasing degree at higher pressures, as was stated above. However, the relatively small percentage increases in reaction rate indicate that, in the range of temperatures studied, the oxidation reaction is not too temperature-sensitive.

Figure 8 shows the variation of phenol conversion with residence time. At pressures above 1500 psig there is almost no change in the degree of conversion with residence time, while at lower pressures conversion drops as residence time decreases. This indicates that the reaction occurs more rapidly at high pressure and indeed the residence time could likely be reduced to just a few minutes without experiencing a significant drop in conversion.

If a "resistances in series" reaction control mechanism is considered (see Appendix) all of the data points for one temperature and air flow rate should fall on a curve, the shape of which will give an indication of the reaction order. Figures 9 and 10 are the curves for 200°C and 250°C, respectively. The data points shown were calculated from experimental data, while the curve in each case is $y = mx^2 + b$, as is indicated in the Appendix. The intercept is the reciprocal mass transfer product and the slope is the reciprocal reaction rate constant. The data points fit quite well to the second order equation curve, indicating that the oxidation reaction is approximately second order with respect to

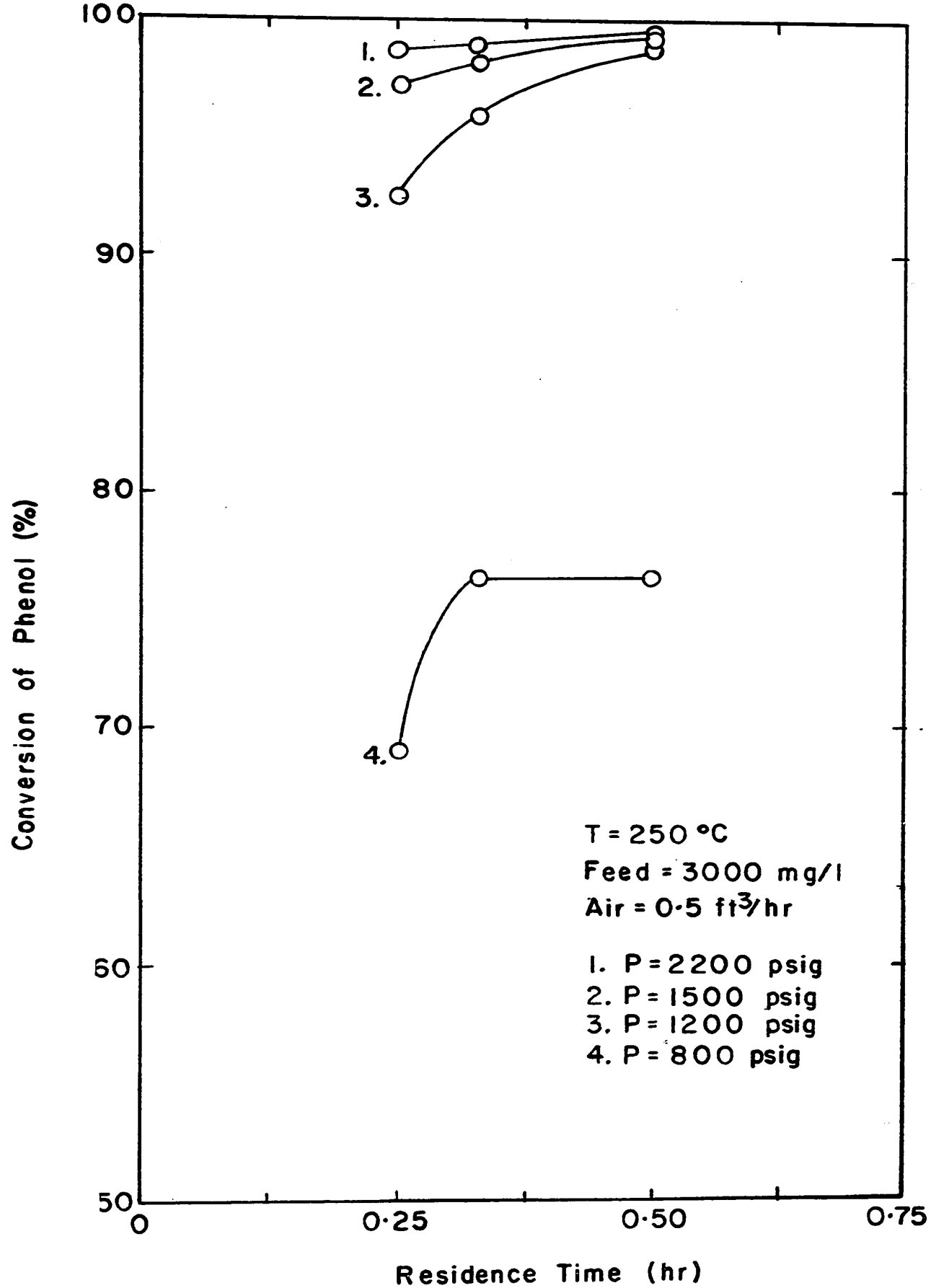


Figure 8. Conversion vs. Residence Time for Different Pressures

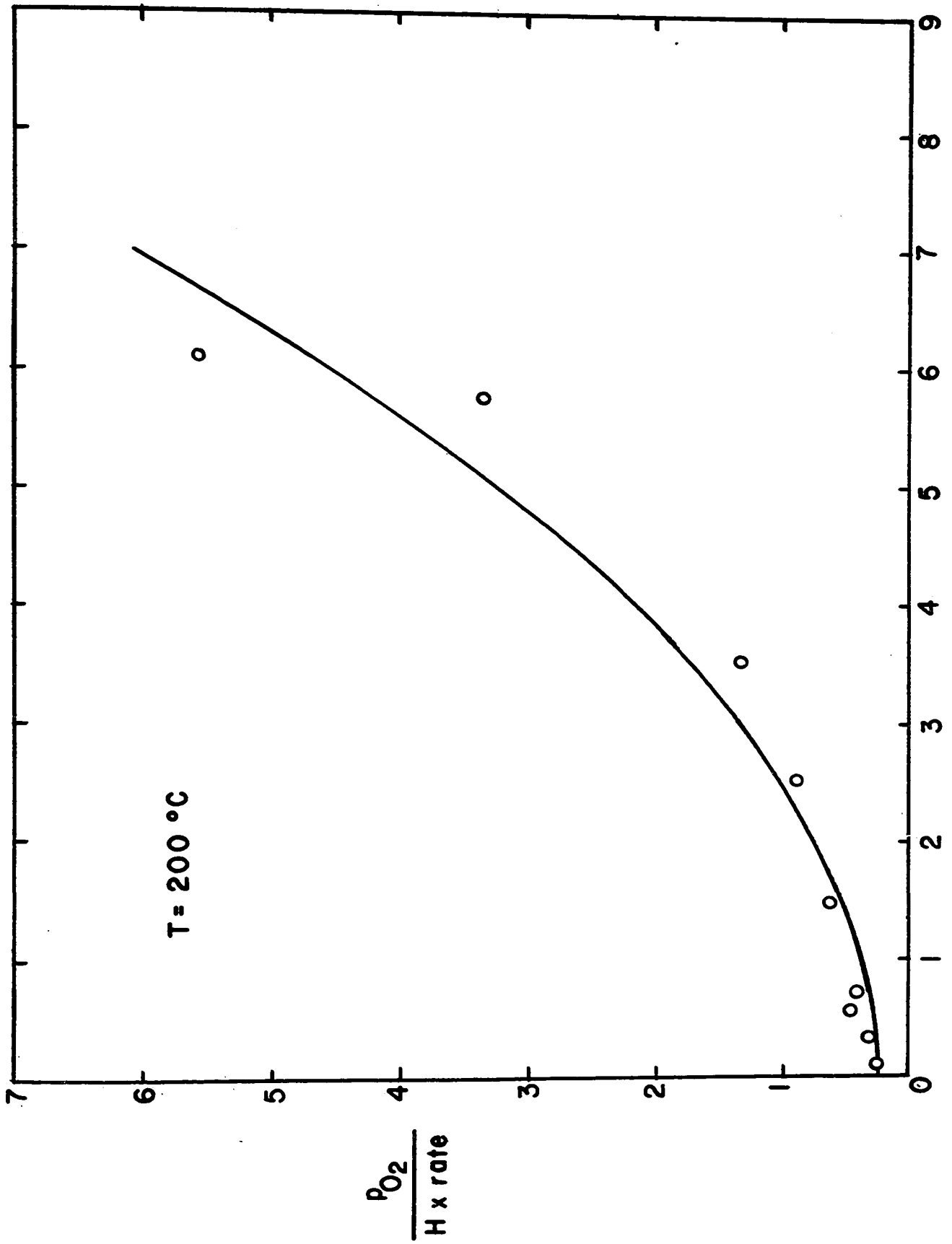


Figure 9. "Resistances in Series" Reaction Control Mechanism at 200°C

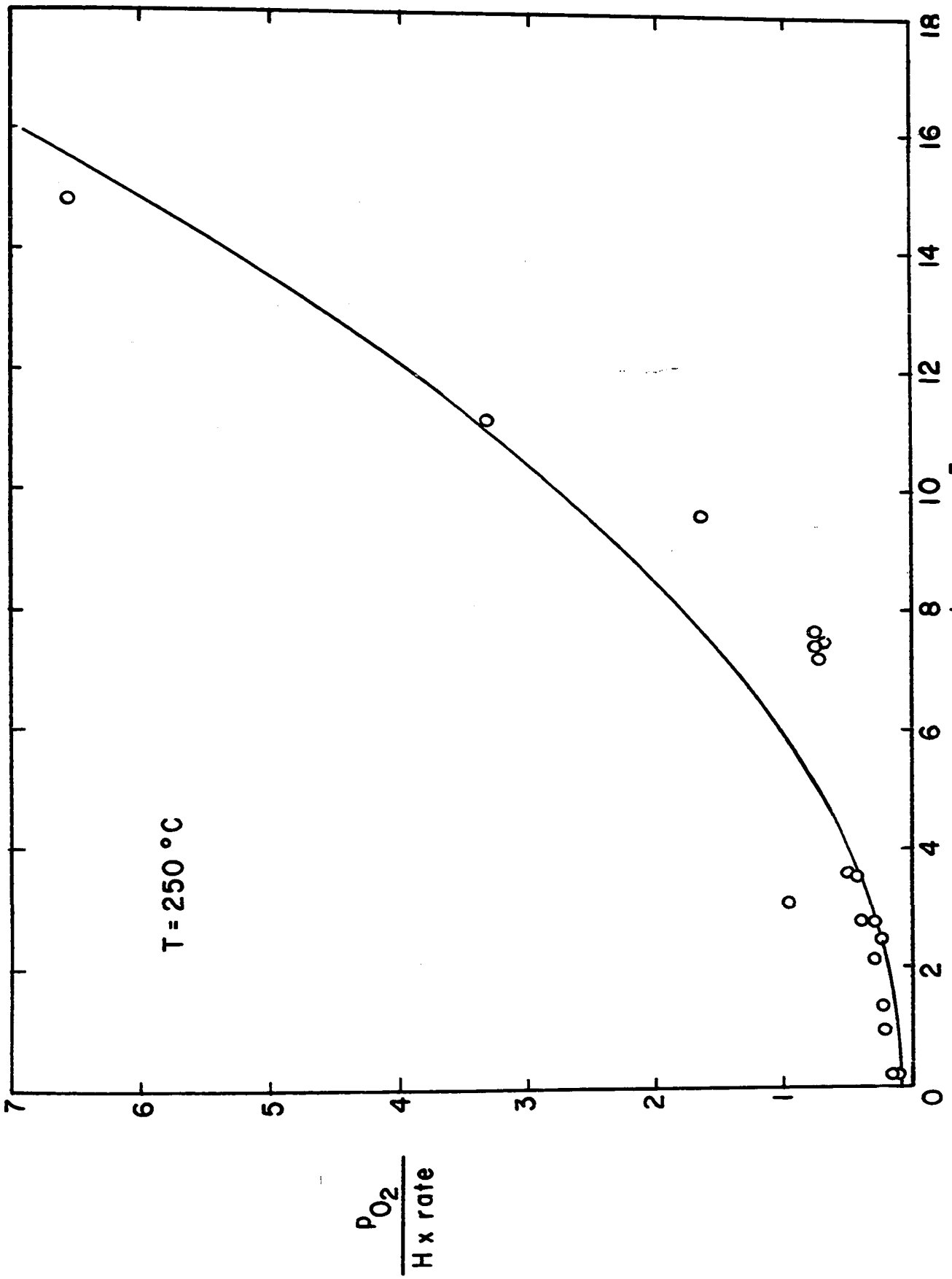


Figure 10. "Resistances in Series" Reaction Control Mechanism at 250°C

phenol.

At 200°C and lower pressures some acetic acid production was noted on the phenol analysis chromatograms. Injections of an acetic acid solution confirmed that the small peaks observed did represent acetic acid. The concentration of acetic acid was estimated to be 50-100 mg/l at most. At 250°C and at higher pressures the production of acetic acid was negligible. In contrast with these results Shmidt[9] found as much as 6000 mg/l acetic acid in his treated water. He also found that formation of acetic acid at 200°C was much greater than at other temperatures. The relatively large amounts of acetic acid found by Shmidt are principally due to the fact that his phenol feed concentrations were about ten times those used in this work.

C.O.D. analyses on the feed and effluent of a run at 250°C and 2200 psig showed that there was a 95.5% reduction in C.O.D. from 7304 mg/l to 336 mg/l, while the phenol concentration was reduced from 3085 mg/l to 14.8 mg/l, a 99.52% reduction. The theoretical C.O.D. of the phenol in the effluent was 35.3 mg/l, and the remaining oxygen demand was created by the small amount of phenol tars which was formed. Shmidt reported that in runs in which he achieved 99.99% phenol removal, to about 3 mg/l, his degree of C.O.D. removal was about 98% (to 1800 mg/l). The formation of tars and other soluble by-products must have been more serious than in this work because a phenol concentration of 3 mg/l

represents a theoretical oxygen demand of about 7 mg/l, and so the remaining portion of the 1800 mg/l C.O.D. must have been contributed by the by-products.

The gas analysis on a run similar to the one discussed above showed that both CO_2 and CO were formed during the reaction. The CO_2 produced was 0.333 scfh, or 0.86% of the gas, while the CO produced was 0.012 scfh, a concentration of 317 ppm. The formation of a small amount of CO was expected on the basis of Shmidt's results, even though Zimmermann had found no traces of it. This indicates that for phenol, even though considerable excess air is provided, the tendency to form some CO under what would seem to be ideal oxidation conditions is not supressed completely as it is with other oxidizable materials such as pulp or sewage wastes. A material balance on this run showing a carbon recovery of 98.6% is included in the Appendix.

Based on the above results it is possible to choose operating conditions which are best suited to the removal of phenol from waste waters. The higher temperature and pressure conditions definitely give the best results as they combine a high percentage of phenol converted with the least amount of undesirable by-products, tars and acetic acid. Because of the small amounts of by-products the plant effluent would have only a faint brownish tinge and little odour. Operating at 300°C instead of the 250°C maximum used in this work would likely provide an even cleaner effluent with a higher

percentage of phenol coverted. This statement is based on Shmidt's results.

Direct comparison of the results obtained in this work with those of Shmidt is not possible without an analysis which would take into account the two different types of reactors used. However, under identical operating conditions the phenol conversion and percentage C.O.D. removal are essentially the same. This proves that the oxidation of phenol can be conducted satifactorily on a continuous basis in apparatus which is not complex.

Several fectors must be considered when the commercialization of the wet air oxidation process for phenol removal is discussed. In Zimmermann's work the feed solutions contained as much as 11.4% by weight oxidizable material while in this work the solutions contained no more than 0.3% phenol. Zimmermann's publications stress that the production of excess steam is an asset of the process but this does not hold true with low feed concentrations because, even though the oxidation is exothermic, there is not enough heat released to vaporize significant quantities of water. The oxidation of phenol in dilute solutions would thus be a net consumer of energy. However in a situation where both the volume of waste water and the concentration of pollutants varied a great deal and where a low and constant effluent concentration was required, the wet

air oxidation process would be an alternative to be considered because of its relative insensitivity to residence time and feed concentration, which has been discussed previously.

There are, of course, many possible combinations of operating conditions and processes which would be satisfactory for dealing with a given pollution situation. For example, a wet air oxidation unit could be operated at a moderate pressure in series with another type of process such as a catalytic converter. A catalytic process such as the one patented by Pope[11] would be especially useful because it would handle both gas and liquid effluents and would convert any CO in the gas as well as products such as acetic acid which display resistance to non-catalytic oxidation. The final choice would have to be based on factors such as equipment reliability, familiarity with the process, desired effluent purity, and economics.

CONCLUSIONS AND RECOMMENDATION

1. The wet air oxidation process has been applied to the continuous oxidation of phenol in dilute solutions and has been shown to be effective in converting up to 99.5% of the phenol, mostly to carbon dioxide and water. A material balance showed a carbon recovery of 98.6%.

2. The results obtained in this work correspond closely to those obtained in an earlier batch reactor study[9] and they show that the application of the process in a continuous flow system, in particular in a continuous stirred tank reactor, is both feasible and workable, with possible applications in the field of water pollution control.

3. The reaction control mechanism is complex. The results indicate that at pressures of 1200 psig and less the rate of mass transfer of oxygen to the reaction site is important in this reactor, while at higher pressures the low concentration of phenol in the reactor (due to high conversion) has more effect on the overall rate. This is important when a reactor is being specified, since chemical reaction control makes the purchase of an agitator unnecessary.

4. It is recommended that further study of the wet air oxidation process be carried out. Three possible goals of such research could be: (i) to learn more about the kinetics of the oxidation reaction and possibly develop a rate expression, (ii) to make a

detailed engineering study of the application of the process to a specific pollution problem in order to determine if the process is attractive for industrial pollution control, and (iii) to confirm conclusion #3 in an actual mixed reactor before full scale use of the process.

APPENDIX

A. TABULATED DATA

The details and results of all experimental runs are tabulated in the following pages.

TABLE 2

SUMMARY OF RUNS 1 TO 10

Run	Liquid Flow (ml/hr)	Feed Concentration (mg/l)	Temperature (°C)	Pressure (psig)	Effluent Concentration (mg/l)	Phenol Conversion (%)	Comments on Run
1	1000	1000	25	2300	1000	0	No air
2	1000	1000	200	1300	1000	0	No air
3	1000	1000	250	1730	1000	0	No air
4	1000	1000	300	2275	1000	0	No air
5	1000	1000	300	erratic	--	--	Compressor Problem
6	1000	1000	300	2280	17	98.3	
7	1000	34000	300	erratic	--	--	Tars Formed
8	200	34000	200	1350	--	--	Tars Formed
9	530	34000	200	erratic	16532	51.4	
10	500	1665	200	1500	995	40.2	Insufficient Air

TABLE 3

SUMMARY OF RUNS 11 TO 28

Gas Flow Rate = 0.5 ft^3/hr at conditions

Run	Liquid Flow (ml/hr)	Feed Concentration (mg/l)	Temperature (°C)	Pressure (psig)	Effluent Concentration (mg/l)	Phenol Conversion (%)	Reaction Rate (g-mole/l-hr)
11	500	1382.5	200	800	--	--	--
12	500	1382.5	200	1450	18.930	98.63	0.007205
13	500	1382.5	200	2300	17.881	98.71	0.007261
14	500	1382.5	250	870	9.610	99.30	0.007305
15	500	1382.5	250	1400	9.737	99.30	0.007304
16	500	1382.5	250	2200	7.336	99.47	0.007317
17	2000	1381.2	200	820	197.361	85.71	0.02519
18	2000	1381.2	200	1510	43.355	96.86	0.02847
19	2000	1381.2	200	2150	30.903	97.76	0.02873
20	2000	1381.2	250	2200	11.395	99.18	0.02915
21	2000	1381.2	250	800	44.415	96.78	0.02845
22	2000	1381.2	250	1490	35.770	97.41	0.02863
23	2000	3049.4	200	810	1039.764	65.90	0.04276
24	2000	3049.4	200	1500	155.591	94.90	0.06157
25	2000	3049.4	200	2220	74.054	97.57	0.06330
26	2000	3049.4	250	2210	14.328	99.53	0.06458
27	2000	3049.4	250	790	717.930	76.46	0.04960
28	2000	3049.4	250	1500	31.037	98.98	0.06422

TABLE 4

SUMMARY OF RUNS 29 TO 38

Gas Flow Rate = 0.5 ft^3/hr at conditions

Run	Liquid Flow (ml/hr)	Feed Concentration (mg/l)	Temperature (°C)	Pressure (psig)	Effluent Concentration (mg/l)	Phenol Conversion (%)	Reaction Rate (g-mole/l-hr)
29	3000	3043.0	250	800	720.614	76.32	0.07413
30	3000	3043.0	250	1500	51.528	98.31	0.09548
31	3000	3043.0	250	2200	30.489	99.00	0.09615
32	4000	3043.0	250	800	947.277	68.87	0.08918
33	4000	3043.0	250	1500	83.492	97.26	0.12594
34	4000	3043.0	250	2200	39.560	98.70	0.12781
35	2000	3050.9	200	1200	345.842	88.66	0.05755
36	2000	3050.9	250	1200	39.900	98.69	0.06406
37	3000	3050.9	250	1200	123.192	95.96	0.09344
38	4000	3050.9	250	1200	229.761	92.47	0.12004

The following runs were done to check on the reproducibility of the data:

45	2000	3084.7	250	2200	15.173	99.51	0.06531
46	2000	3084.7	250	2200	14.812	99.52	0.06532
47	2000	3047.4	250	2200	14.653	99.52	0.07098

TABLE 5

SUMMARY OF RUNS 39 TO 44

Gas Flow Rate = 1.0 ft^3/hr at conditions

Run	Liquid Flow (ml/hr)	Feed Concentration (mg/l)	Temperature (°C)	Pressure (psig)	Effluent Concentration (mg/l)	Phenol Conversion (%)	Reaction Rate (g-mole/l-hr)
39	3000	2479.9	250	800	218.082	91.21	0.07219
40	3000	2479.9	250	1200	32.253	98.70	0.07812
41	3000	2479.9	250	1500	28.428	98.85	0.07824
42	4000	2479.9	250	800	450.279	81.84	0.08636
43	4000	2479.9	250	1200	111.598	95.50	0.10078
44	4000	2479.9	250	1500	59.023	97.62	0.10302

TABLE 6

PARTIAL PRESSURES OF OXYGEN

Temperature (°C)	200	250	300
Vapour Pressure of Water (psia)	225	576	1246

The table below is based on

$$p_{O_2} = 0.21\ (P_{TOT} - p_{H_2O})$$

Total Pressure (psia) \ Temperature (°C)	200	250	300
815	124	50	---
1215	208	134	---
1515	271	197	56
2215	418	344	203

NOTE: The partial pressures of oxygen used are those at the reactor inlet rather than at the outlet. This was done because the amount of air supplied was always much greater than the amount required for reaction, and so the outlet oxygen concentration was assumed to be the same as the inlet value (see Appendix B-2, p. 50-51).

B. CALCULATION METHODS

1. Stoichiometry

The balanced equation for the complete oxidation of phenol is

$$C_6H_5OH + 7O_2 \longrightarrow 6CO_2 + 3H_2O$$

The molecular weight of phenol is 94. The theoretical oxygen demand of a phenol solution of concentration c mg/l is

$$\frac{c}{94} \times 7 \times 32 = 2.4\ c \text{ mg/l.}$$

2. Calculation of Air Requirement

Consider the air requirement for a run with the following conditions:

feed concentration	3000 mg/l
feed rate	4000 ml/hr
temperature	250 °C
pressure	2200 psig

From above, the theoretical oxygen demand of this solution is 7140 mg/l. Since the flow rate is 4.0 l/hr, the oxygen requirement is

$$7.14 \times 4.0 = 28.56 \text{ g/hr.}$$

Since air is approximately 23.3% by weight oxygen, the air rate must be

$$\frac{28.56}{0.233} = 122.6 \text{ g/hr.}$$

The density of air at 25°C and 14.7 psia is 0.00141 g/cm^3. The flow rate of air required is thus

$$\frac{122.6}{0.00141} = 86950 \frac{cm^3}{hr} = 3.1 \frac{ft^3}{hr} \text{ at } 25^\circ C, 14.7 \text{ psia.}$$

The air supplied (0.5 ft^3/hr at conditions) was

$$0.5 \times \frac{298}{523} \times \frac{2215}{14.7} = 42.9 \frac{ft^3}{hr}.$$

It can be seen that considerable excess air was present.

3. Calculations to Check on Shmidt's[9] Claim of Excess Air

Shmidt claimed to have 30-50% excess air present in each run, but it can be shown that this may not always have been true. He used liquid samples of 100-500 ml and filled the remainder of his 1-litre reactor with compressed air. The following conditions are typical of those used by Shmidt: 300°C, 155 atm, 34000 mg/l feed concentration.

At 300°C, the vapour pressure of water = 1235 psia
= 84 atm.

Therefore, initial air pressure in reactor = 155 - 84
= 71 atm.

Two sample sizes will be considered at these conditions.

(a) Liquid = 100 ml, Gas = 900 ml.

At 25°C, the air supplied is $n = \frac{PV}{RT} = \frac{71 \times 0.90}{0.082 \times 298}$
= 2.62 g-mole

which contains 0.21 x 2.62 = 0.55 g-mole O_2.

The phenol present is $\frac{34 \times 0.10}{94} = 0.036$ g-mole.

From stoichiometry, 7 moles of O_2 are needed per mole of phenol, i.e. 0.55 g-mole O_2 can convert 0.079 g-mole phenol. Thus there is 117% excess air in this case.

(b) Liquid = 500 ml, Gas = 500 ml.

At 25°C, $n_{air} = \frac{71 \times 0.50}{0.082 \times 298} = 1.46$ g-mole

$$n_{O_2} = 0.21 \times 1.46 = 0.31 \text{ g-mole}$$

$$n_{phenol} = \frac{34 \times 0.50}{94} = 0.18 \text{ g-mole}$$

From stoichiometry, 0.31 g-mole O_2 can convert 0.044 g-mole phenol.

In this case there is insufficient air.

4. Calibration of the Chromatograph for Phenol Analysis

The chromatograph was left on at all times to ensure that it was operating at steady state. The operating conditions were:

injector temperature	209°C
column temperature	142°C
detector temperature	207°C
chart speed	12 in/hr
range	10^{-11} amp/mv
attenuation	4

Concentration of calibration solution = 982.04 mg/l (note that milligrams/litre ≡ nanograms/microlitre).

Results of one injection:

sample volume = 1.20 μl
weight of phenol = 982.04 x 1.20 = 1178.45 ng
peak weight = 0.03652 g

$$\text{Standardization Value} = \frac{\text{weight of phenol (ng)}}{\text{weight of peak (g)}}$$

$$= 3.23 \times 10^4 \text{ ng phenol/g paper}$$

This procedure was repeated several times and an average result was taken. Thus,

average S.V. = 3.31×10^4 ng phenol/g paper

for an attenuation of 4.

For different attenuations the S.V. is multiplied by the ratio of the new attenuation to 4.

5. Phenol Analysis Results

The phenol peaks on the chromatograms were cut out and weighed and the Standardization Value was used to determine the phenol concentration in the samples.

As an example, consider run #16:

feed concentration = 1382.5 mg/l
liquid feed rate = 500 ml/hr

Results of one injection:

sample volume = 1.65 μl
peak weight = 0.00035 g
phenol concentration = $\frac{\text{peak weight x S.V.}}{\text{sample volume}}$
= 7.02 mg/l

The average concentration for all injections was 7.34 mg/l.

Percentage conversion = $\frac{1382.5 - 7.34}{1382.5} \times 100\%$
= 99.47%

Phenol flow in = 1382.5 x 0.50 = 691.25 mg/hr
= 0.007356 g-mole/hr

Phenol flow out = 7.34 x 0.50 = 3.67 mg/hr
= 0.000039 g-mole/hr

Reaction rate (based on volume of reactor) =

$$\frac{0.007356 - 0.000039}{1} = 0.007317 \ \frac{\text{g-mole}}{\text{l-hr}}$$

6. Carbon Dioxide Analysis

The column and operating conditions used are discussed in the "Experimental" section. The column was calibrated using a calibration gas which contained 1.06% CO_2 by volume. The chromatograph was equipped with a 3 ml sample loop so it was not necessary to use a syringe

to inject samples. The chromatograms were analyzed using the "cut and weigh" method.

For the calibration gas, the average peak weight was 0.03030 g. Thus,

$$\text{Standardization Value} = \frac{1.06}{0.0303} = 34.98 \ \frac{\%CO_2}{\text{g paper}}$$

The following calculations were for run #47.

For the air supply, average peak weight = 0.00110 g, and so the air was 0.0385 % CO_2.

For a gas sample, average peak weight = 0.02581 g, and so the effluent gas was 0.903 % CO_2.

CO_2 produced in reaction = 0.903 - 0.0385 = 0.865 % of gas.

The gas flow rate was 0.5 ft^3/hr at conditions (i.e. 38.54 scfh), so CO_2 produced in reaction =

$$0.00865 \times 38.54 = 0.333 \text{ scfh.}$$

7. Carbon Monoxide Analysis

The same sample loop and chromatograph were used for CO analysis as were used for CO_2 analysis. The calibration gas was 0.97 % by volume CO in nitrogen.

For the calibration gas, the average peak weight was 0.02200 g. Thus

$$\text{Standardization Value} = \frac{0.97}{0.02200} = 44.09 \ \frac{\%CO}{\text{g paper}}$$

at attenuation 2.

The following calculations were for run #47.

No CO was detected in the air supply.

For a gas sample, at attenuation 1, the average peak

weight was 0.00144 g, and so the effluent gas was

$$0.00144 \times 44.09 = 0.0317\ \%\ CO, \text{ or } 317 \text{ ppm.}$$

The gas flow rate was 0.5 ft^3/hr at conditions (i.e. 38.54 scfh), so CO produced in reaction =

$$0.000317 \times 38.54 = 0.0122 \text{ scfh.}$$

8. Material Balance for Run #47

Phenol feed concentration = 3047.4 mg/l

Liquid feed rate = 2200 ml/hr

Therefore, phenol feed rate = $2.200 \times 3.047 = 6.703$ g/hr

Conversion of phenol was 99.52 %, i.e. 6.671 g/hr were converted.

CO_2 production was 0.333 scfh.

Density of CO_2 at 25°C, 1 atm = $1.811 \frac{g}{l} = 51.279 \frac{g}{ft^3}$

Thus, CO_2 produced in reaction = $0.333 \times 51.279 = 17.076$ g/hr

Based on stoichiometry, this represents a consumption of

$$17.076 \times \frac{94}{264} = 6.080 \frac{\text{g phenol}}{\text{hr}}.$$

CO production was 0.0122 scfh.

Density of CO at 25°C, 1 atm = $1.145 \frac{g}{l} = 32.419 \frac{g}{ft^3}$

Thus, CO produced in reaction = $0.0122 \times 32.419 = 0.396$ g/hr

Based on stoichiometry, this represents a consumption of

$$0.396 \times \frac{94}{168} = 0.222 \frac{\text{g phenol}}{\text{hr}}.$$

Total phenol converted to gaseous products = $6.302 \frac{g}{hr}$.

This leaves 6.671 - 6.302 = 0.369 g/hr phenol which was

converted to by-products such as tar and acetic acid. This fact is confirmed by the characteristics of the effluent: it had a slight brownish discoloration and had a slight odour of acetic acid.

A quantitative confirmation is given by the results of the C.O.D. analysis: the effluent C.O.D. = 336 mg/1. Therefore, C.O.D. due to phenol unconverted =

$$14.652 \times 2.38 = 35.90 \text{ mg/1.}$$

Now, the 0.369 g/hr of phenol which was converted to tars and acid represents a concentration of 168 mg/1 phenol. The theoretical oxygen demand of this would be

$$168 \times 2.38 = 400 \text{ mg/1.}$$

Since the dichromate C.O.D. method does not pick up acetic acid, the measured C.O.D. of 300.9 mg/1 for the by-products is very reasonable.

A carbon balance shows:

carbon in (as phenol) = $6.703 \times \frac{72}{94} = 5.134 \frac{g}{hr}$

carbon out - as CO_2 = $17.076 \times \frac{12}{44} = 4.658 \frac{g}{hr}$

- as CO = $0.396 \times \frac{12}{28} = 0.170 \frac{g}{hr}$

- as C.O.D. (assumed as phenol)

$0.336 \frac{g}{1} \times \frac{1}{2.38} \times 2.2 \frac{1}{hr} \times \frac{72}{94}$
$= 0.236$ g/hr

Total carbon out = 5.064 g/hr

Percentage recovery = $\frac{5.064}{5.134} \times 100\ \% = 98.6\ \%$.

This assumes that the C.O.D. of tars is the same as that of phenol. In fact the tars will probably be partly oxygenated, which will reduce the C.O.D. However, since some acids, notably acetic acid, are not picked up by the C.O.D. analysis, this allows for the assumption made above.

9. The "Resistances in Series" Reaction Control Mechanism

The overall reaction control mechanism involves both mass transfer and chemical reaction, and these effects can be combined and studied together. The equation for mass transfer is (with the rate in mole/hr)

$$\text{rate} = k\, a\, V\, (c^* - c_L).$$

Assuming a first order relationship for phenol, the chemical reaction equation is

$$\text{rate} = k_R\, V\, c_L\, c_{\text{phenol}}.$$

Since the two rates are identical these equations can be combined by eliminating c_L to give

$$\text{rate} = \frac{c^*}{\frac{1}{ka} + \frac{1}{k_R c_{\text{phenol}}}}.$$

Using Henry's Law and inverting, this becomes

$$\frac{p_{O_2}}{\text{rate} \times H} = \frac{1}{ka} + \frac{1}{k_R c_{\text{phenol}}}.$$

This equation can be plotted and it will indicate the true dependence of rate on phenol concentration. To be completely general it would have been better to assume an n^{th} order relationship above, but the assumption of

first order merely simplifies the mathematics.

A small computer program was written to do the calculations and it was combined with a least squares fit program. The Henry's Law constant data were taken from Himmelblau[12] and all other rate and concentration data from Tables 2 to 5.

The results of the computations at 200°C and 250°C are plotted in Figures 9 and 10 respectively (see Results and Discussion). The curves are least squares fits of the data and are based on slopes and intercepts calculated by the program. It can be seen from the Figures that the reaction is definitely not first order in phenol concentration, but is closer to second order, as the curve plotted in each case is $y = mx^2 + b$.

The correlation coefficients computed by the program were, for a linear relationship, 0.9149 for 200°C and 0.9160 for 250°C. Similarly, for a second order equation they were 0.9649 and 0.9610 respectively. For third and fourth orders at 250°C the coefficients were 0.9597 and 0.9763, so it can be seen that using an order higher than second is of no advantage. The standard estimate of error for the 250°C curve was 0.8834.

The slope of each curve is the reciprocal of the reaction rate constant, and the intercept is the reciprocal of the mass transfer product.

The activation energy E can be estimated from the two slopes:

$$\text{at } 250^\circ\text{C, slope} = \frac{1}{k_R} = 2.66 \times 10^{-8}$$

$$k_R = 3.76 \times 10^7$$

at 200°C, slope = 1.19×10^{-7}

$$k_R = 8.40 \times 10^6$$

Using Arrhenius' equation,

$$k_R = k_{Ro} \exp(-E/RT),$$

the activation energy is calculated to be

$$E = 14{,}857 \text{ cal/mole}$$

and this is a reasonable value for this type of reaction[19].

The increase in mass transfer coefficient with temperature can also be estimated. The intercepts from Figures 9 and 10 are, respectively, 0.25 and 0.10. Thus

at 250°C, $\frac{1}{ka} = 0.10$ and $ka = 10$, and

at 200°C, $\frac{1}{ka} = 0.25$ and $ka = 4$

so $k_{250}/k_{200} = 2.5$.

The mass transfer coefficient can be estimated from[16]

$$k \propto D\,(Re)^{0.5}\,(Sc)^{0.33}.$$

Reducing all terms to the relevant variables T, μ, and ρ, (using the Stokes-Einstein equation), we get

$$k \propto \frac{T^{0.667}}{\mu^{0.837}} \times \rho^{0.167}.$$

Inserting the corresponding values in the above relationship gives

$$k_{250}/k_{200} = 2.64.$$

This result compares favorably with estimate above.

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