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LA THÈSE A ÉTÉ
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WET AIR OXIDATION OF PHENOL
AT ELEVATED TEMPERATURES AND PRESSURES

by

FARHAD MOSAVAT

A thesis submitted to the
School of Graduate Studies
in partial fulfillment of the
requirements for the degree of

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Farhad Mosavat, Ottawa, Canada, 1982.

ABSTRACT

The Wet Air Oxidation process was carried out on an aqueous phenol solution in a continuous stirred tank reactor. The range of operating conditions was - temperature: 25-250 °C, pressure: 800-2,200 psig, feed concentration: 1,200-4,500 mg/l and liquid residence time: 0.36-1.4 hour.

The effect of process variables: temperature, pressure, liquid flow rate, air flow rate, and agitation speed on the gas holdup ratio in the reactor was also studied. In this part distilled water was used as the liquid feed to the reactor, while other conditions remained unchanged.

The reaction did not proceed at temperatures below 120 °C. At 200 °C some tar formation reactions were noticed and among the products Diphenyl Ether was identified. The tar formation decreased with increasing pressure and temperature.

Phenol conversion in some runs was as high as 96.83%. The oxidation reaction rate at higher pressures was controlled more by chemical reaction than by mass transfer and the role of mass transfer became more significant at lower pressures.

ACKNOWLEDGEMENTS

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NOMENCLATURE

| | |
|-----------------|--|
| a | Interfacial area, m^2/m^3 |
| α | A parameter in Equation (5) |
| b | Stoichiometric ratio of moles of phenol to oxygen |
| δ | Correction factor for phenol concentrations |
| C^* | Saturation oxygen concentration in liquid, moles/l |
| C_{O_2} | Oxygen concentration in liquid, moles/l |
| $C_{Ph(0)}$ | Initial or feed concentration of phenol in liquid, moles/l |
| C_{Ph} | Phenol concentration in reactors liquid phase, moles/l |
| ΔC_{Ph} | Concentration change of phenol inside reactor, moles/l |
| E | Activation energy, cal/gm mole |
| H | Distribution coefficient in Henry's Law, atm. l/mole |
| k_l | Liquid phase mass transfer coefficient, m/hr. |
| k_r | Chemical reaction rate constant, moles/hr. l |
| L | Liquid flow rate, l/hr. |
| m | An exponent in chemical rate equation |
| n | An exponent in chemical rate equation |
| N_w | Number of moles of water, moles |
| N_{air} | Number of moles of air, moles |
| N_T | Total number of moles, moles |
| P | Total pressure of reactor, atm. |

| | |
|------------------|---|
| P_{O_2} | Partial pressure of oxygen, atm. |
| \overline{P}_W | Vapor pressure of water, atm. |
| r | Rate of reaction, moles/hr. |
| R | Gas law constant, cal/gm mole °K |
| ρ | Liquid density, gm/cm ³ |
| s | Degree of saturation of gas phase with water, percent |
| T | Temperature, C or K |
| τ | Liquid residence time in the reactor, hr. |
| V_{air} | Volumetric air flow rate, l/hr. |
| V_G | Volume of gases inside the reactor, l |
| V_L | Volume of liquid inside the reactor, l |
| V_R | Reactor volume, l |
| x | Rate of water evaporation inside the reactor, moles/hr. |
| y | Rate of water condensation inside condenser, l/hr. |

INTRODUCTION

Water pollution has long been associated in the public's mind with nauseous smells, ugly sights and with loss of recreational opportunities. Many people are vaguely aware that the same water-bodies that the polluters use as their private sewers often do double duty as the source of many food items, including the most important food-stuff; drinking water. An estimated one half the U.S. population drinks water only hours after it is discharged from some industrial or municipal sewer. Still, until very recently, it has been widely assumed that serious hazards caused by water pollution were a relic of past centuries, before the wide spread use of chlorination and the technology of drinking-water purification. Such comforting notions are mistaken. Available evidence points increasingly to water pollution as a possible contributor to many human ailments, including heart disease, cancer, birth deformation, and genetic damage.

Poisons like arsenic, lead, or methyl mercury, for example, can produce damage to the brain and the central nervous system which may not show up for several years and which may be easily misdiagnosed when it does appear. The above poisons have been found in water in measurable amounts.

Beyond damage to human health are the more measurable indices of increasing water pollution. Six million fish were recorded killed

by pollution in U.S. in 1960; the number had reached to 23 million in 1970. Mercury pollution has lead to warnings and restrictions on sport and commercial fishing in Canada and many states in the U.S. Furthermore the annual economic loss from water pollution in the U.S. was placed at nearly \$13 billion in 1968.

The drinking-water treatment technology now being used is typically not capable of screening out many of industry's exotic new pollutants. Little is known about most of the 12,000 toxic or potentially toxic chemicals now being used by industry. An estimated 500 new chemicals are introduced each year, with little or no information provided to an unsuspecting public about the dangers of their disposal into the environment. Thus the organic compounds have a great role in the water pollution problem, and make it more complex as they vary quantitatively and qualitatively as a result of new industrial units and processes.

The apparent need for new techniques lead to the development of different methods in the treatment of waste streams. Among the methods for removing organic materials in water, adsorption-filtration, ozonation, catalytic oxidation, biochemical oxidation, evaporation-incineration, and wet air oxidation are being considered more as a result of their flexibility.

A newly developed adsorption-filtration process using activated carbon is now being used by Rhodia Inc.¹, Portland, Oregon. It has succeeded in stripping dangerous levels of toxic phenols from wastewater flowing from its herbicide plant and meets the state-prescribed

maximum limitation of 1.0 mg/lit. Although phenol removal reaches 99% in this plant, (initial concentration is 100 mg/lit), there has not been any work on the applicability of the process to higher initial concentrations and also for removal of other organic compounds having a different type of molecular structure.

Ozone and other peroxides as well as molecular oxygen² has been used for the oxidation of organics in the liquid phase mostly on the investigations on the reaction mechanisms or aiming at desired end products.³ Very high prices of oxidizing agents make these methods unsuitable for the treatment of waste streams.

The biochemical treatment of waste water has been researched extensively resulting in the installation of many such units around the globe. While this method is applicable on biodegradable organic materials, it is not sufficient for all kinds of wastes and also has high investment and operational costs. The total sum of daily operating and capital costs of an activated sludge unit⁴ (5gm/l initial BOD, 90% BOD reduction) is listed as \$2,340*, while for WAO unit (200 gal/min., 120 gm/l initial COD, 95% reduction) is \$1,540*. Hence wet air oxidation process operates at significantly less expenses.

A comparison of evaporation-incineration and wet air oxidation methods by Ontario Research Foundation⁵ shows the wet air oxidation as a more satisfactory alternative for the treatment of domestic and industrial wastes.

The wet air oxidation process, as an alternative, is able to process a wide-range of organic waste streams with equal ease and

*The values are based on 1972 prices.

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complete assurance of a disposable nuisance-free residue. There is no air pollution, objectionable odor, fly ash or soot because the operation is completely enclosed. The wet air oxidation process has also been used for recovery of inorganic chemicals⁴ (Chromium, in treatment of sludge from glue manufacture). It has also been proposed for processing ores in the mining industry⁴ where the slurried ores can be wet oxidized, where the sulfides would be converted to sulfates without any air pollution problem and abnoxious sulfur emissions.

In this study the wet air oxidation of a typical organic water-pollutant, phenol, is investigated. Phenol is a toxic compound which causes severe burns on direct contact to the skin and can be detected in the waste streams of steel mills, petrochemical plants and oil refineries. Phenol⁶ produces a medicinal taste and odor to drinking water which can be detected in very low amounts (50-100 p.p.b.). It's detection by taste is even more sensitive in chlorinated waters. Phenol is a powerful bacteriacide and in high concentrations (200 p.p.m. or more) can cause deactivation of biological oxidation treatment plants by killing the bacteria. Chronic phenol poisoning,⁷ following prolonged exposure to low concentrations of the vapor or mist, results in digestive disturbances (vomiting, difficulty in swallowing, excessive salivation, diarrhea, loss of appetite), nervous disorders (headache, fainting, dizziness), mental disturbances and skin eruption. Legislative antipollution laws limit the presence of phenol in waste streams dischargeable into natural waterways in a 0.02-2.0 p.p.m. range.

LITERATURE SURVEY

1. Process Background

Generally the process of complete oxidation of organic matter with air to produce carbon dioxide and water, under elevated temperature and pressure, in the presence of liquid water is referred to as "Wet Air Oxidation" or "Wet Air Combustion".

The basic process⁵ was patented in 1905 for the treatment of sulphite liquor from wood pulp production and in 1927 for the treatment of metallurgical ores.

The idea of employing Wet Air Oxidation (WAO) to treat waste streams was first proposed by Zimmermann⁸ in 1944 in the U.S. and patented as the Zimmermann Process.⁹ The patent later resulted in the installation of the first WAO unit in the Metropolitan Sanitary District of Greater Chicago in 1957. The number of WAO units installed in different countries around the globe reached 70 by 1972⁵ and the recent escalation of energy costs is bringing about a resurgence of interest in this technique.

In the studies by Zimmermann,⁴ the process has been applied to waste streams of paper mill effluents, dairy wastes, sewage sludges, slaughter house effluents, and oil refinery wastes. The results have shown that the final chemical oxygen demand (COD) of the treated sludges was independent of the initial COD for oxidation temperatures

over 250 °C, and the COD removal was as high as 90 percent in a continuous process having a contact time of one hour. The study covered the temperatures of 25 to 300 °C, and showed that the oxidation rate at lower temperatures (less than 150 °C) was too slow for any practical application, although complete oxidation was possible as low as 150 °C. Also the degree of COD removal was dependent on such factors, as the temperature at which the oxidation takes place, the residence time in the reactor, the quantity of air used per unit of sludge, and the concentration of oxidizable material in the sludge. In his study Zimmermann used a fixed pressure of 1,200 psig, and did not discuss the effects of the total pressure of the reactor on the percentage removals of COD. He also concluded that the reaction proceeded only when liquid water was present, and usually stopped when it was not.

Looking for the possible use of the WAO process for the treatment of waste streams from naval ships, an investigation was conducted by Shatzberg¹⁰ et al. in 1974 on six different waste feeds to a batch reactor. The percentage reduction in C.O.D. versus time for two temperatures (500 °F and 600 °F) were studied on all feeds, using air and also molecular oxygen. Over the range of variables studied in this work (rather typical of WAO), the percentage reduction in COD using molecular oxygen was almost the same as in the case of air oxidation. Thus confirming Zimmermann's¹¹ claim that WAO could be generally operated without excess air. The effects of the pH of the solution was also studied and showed the process was insensitive to

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small and even large changes of the pH of the solution.

2. Application to Phenol Oxidation

The wet air oxidation of phenol was studied by Schmidt¹² in a batch system. A very high degree of conversion was reached (99.9%) at a temperature of 300 °C, pressure of 155 atm., and a contact time of one hour. He obtained some carbon monoxide as well as dioxide as end products. The carbon monoxide was believed to be due to the insufficient amount of air present.¹³ There were also some other refractory products formed in his work such as acetic acid and formic acid, but the C.O.D. removal in the experiments was as high as 98.4%. Schmidt found a dark colored liquid at lower temperatures (< 200 °C) but did not discuss it further.

An early study was made by Schulze and Hasse¹⁴ in Germany on the aeration of the waste water containing phenols. The study was made at atmospheric pressure and temperatures around room temperature, and showed a rather high percentage removal. At 80-90 °C, for samples of 1500 mg/l initial concentration (C_0) the percentage removal was 98%, the increase in C_0 decreased the conversion which was 60%, and 27% for C_0 in the ranges 10,000-26,000 and 26,000-28,000 mg/l respectively for a one hour contact time. They found two parallel reactions involved in the separation of phenols: one reaction was the polymerization of lower phenols to heavy soluble condensation products which was more rapid at higher temperatures (close to 100 °C) and the other was the complete oxidation reaction at lower temperatures.

Their conclusion can be explained by the fact that they did not study the oxidation reaction at higher temperatures than 100 °C where the polymerization reaction actually stops and the complete oxidation becomes very significant. The study covered the pH range of highly acidic to highly basic solutions and results showed that the polymerization reaction was best achieved in pH range of 8-10. For the case of highly acidic waste water solutions; a large decrease in phenol concentration was noted which was believed to be partly due to the evaporation of phenol into the air.

The WAO process has also been studied by Russian workers. In the work of Stepanian et al.,¹⁵ solutions of phenol, methanol, and formaldehyde were processed in a semi-batch reactor at a temperature of 200 °C and pressure of 40 atm., either as a mixture or as single component solutions. The C.O.D. removal was found to be 80%. The contact time was 1.5 hour for all experiments. The results obtained by this work were essentially similar to the previous work of Zimmermann.

Another related study in Russia by Kramarenko,¹⁶ covered samples of four different categories of substances:

1. Volatile at 300 °C and soluble in water,
2. Volatile but insoluble in water,
3. Non-volatile but soluble in water,
4. Non-volatile and insoluble in water.

In this work it was shown that the mechanism and the kinetics and the phase in which the oxidation of thoroughly soaked organic materials

takes place, depend on the solubility and the volatility of the material, so that the liquid phase oxidation would only happen to the non-volatile substances; a contradiction to Zimmermann's theory to some extent.

A very recent work on catalytic oxidation of phenol in the gas phase by Walsh et al.,¹⁷ confirms that there is not any oxidation reaction in the gas phase when catalyst is not present and even with catalyst present the conversion in the gas phase only would not be as high as it is observed by Zimmermann, Schmidt of other workers in WAO.

A 1974 study by Sadana and Katzer,¹⁸ on catalytic oxidation of phenol in aqueous solutions showed that the catalytic oxidation at atmospheric pressure was quite slow, and nearly two days were required to oxidize 50% of the phenol at the highest catalyst loadings studied. They also showed that the vapor phase oxidation could be done only at higher temperatures (300-400 °C) using catalyst.

The process of WAO was taken under study by Zimpro⁴ Inc., where a continuous unit for municipal sewage sludge was built. The operation of the plant started in 1967, working at 300 psig and 300-400 °F. A COD removal of up to about 80% was obtained in this unit depending on the type of waste material.

Further studies of WAO process in a continuous system were carried out at the University of Ottawa by Ferguson¹³, where the WAO of phenol was studied in a non-agitated reactor. The results showed

that the conversion was a function of pressure, temperature, concentration, and the liquid residence time. An increase in pressure, temperature, and residence time favored the conversion. At pressures close to vapor pressure of water, the conversion was found to be very sensitive to pressure changes. At higher pressures the conversion was unchanged for further pressure increases. It was concluded that the reaction in the high pressure region was chemically controlled. There was also found a trade-off between the operating pressure and the contact time in the high conversion range. In their work the amount of acetic acid formation in comparison to Schmidt's analysis was minimal and conversion of up to 99.53% were reached. The study concluded that in the lower pressure range, to increase the conversion, one should try to increase the mass transfer term k_1 . Thus a similar study in a mechanically agitated reactor was recommended by them.

3. Gas Holdup Studies

Gas holdup ratio is defined as that portion of the reactor volume which is not filled with liquid. To determine the actual liquid residence time in the reactor, some knowledge of gas holdup ratio is essential.

The interfacial area, liquid side mass transfer coefficient, and gas holdup have been studied by Sideman, Hertascu, and Fulton¹⁹. The effect of various variables such as the linear gas velocity,

agitator speed, and power input of the impeller per unit volume of reactor are investigated. The important data on the agitators and vessels used and the range of variables covered by many other investigators are also included. It is obvious that there is a considerable discrepancy in the literature regarding the effect of variables on interfacial area. Thus, the effective interfacial area varies as 0.0 to 1.0 power of gas flow rate, 0.7 to 3.0 power of speed of the agitator, 0.0 to 1.0 power of the gas holdup, and 0.35 to 0.95 power of the power input of the impeller per unit volume of liquid.

Working at atmospheric pressure, Westerterp, Van Dierendonk, and Dekara²⁰ showed that at low impeller speeds, the gas holdup is essentially dependent on gas flow rates, while at high impeller speeds gas holdup depends upon impeller speed. Thus there is a transition region where both the gas flow rate and the impeller speed are important. In this study they also derived an equation to give the prediction of the minimum speed of agitation beyond which only the impeller speed is important.

In the work of Linek²¹ et al. the effect of absorption rate on gas holdup and total interfacial area was studied in a mechanically agitated reactor at atmospheric pressure where the absorption of pure oxygen in sodium sulphite solution in the presence of Cobalt catalyst was used to verify the model concepts. It was found that under certain conditions there was a significant decrease of interfacial area and holdup along with increasing absorption rate. They also

established a relationship which predicts the fractional decrease in the gas holdup and interfacial area as a function of the relative amount of gas absorbed.

Despite the discrepancies existing in the vast amount of data on gas holdups, bubble diameters, and mass transfer rates for aerated mechanically agitated vessels, there has not been any attempt at similar studies at higher than atmospheric pressures until the recent work of Sridhar and Potter²² in 1980.

In their experimental work, Sridhar and Potter studied the effect of system pressure on gas holdup and bubble diameter in a pressurized stirred gas-liquid reactor. The results showed that increasing the pressure would increase gas holdup and decrease bubble diameter. The range of pressures used in this study is 1-10 atm. All the data was obtained using a single reactor. The liquid in the reactor was cyclo-hexane and the gas was air. While the results of this study, still have to be extrapolated for any higher pressure than 10 atm., the use of their study for the purpose of present work remains limited.

In the course of present study it was decided that a separate set of experiments was necessary for obtaining gas holdup ratios at reactor conditions. The details of such experiments are presented in the Appendix.

4. Solubility and Diffusivity Data

There are some data available in the literature on air-water systems. Himmelblau²³ has collected a vast amount of data on the solubilities of inert gases to form a generalized solubility correlation. The data are in the form of graphs of Henry's Law Constant versus reciprocal absolute temperature ($^{\circ}\text{K}^{-1}$). All curves are concave downward which means that there is a maximum value of H for each gas, and this corresponds to a minimum solubility.

St. Denis and Fell²⁴ have correlated the diffusivity of oxygen in water for temperatures of up to 60°C from a large number of sources. These data are more reliable in the study of mass transfer effects, rather than the generalized prediction methods. However, since the WAO process most likely operates at temperatures close to 200°C , the usefulness of these data is limited in this application.

5. Basis for this Thesis

The above mentioned works on the WAO process demonstrate its applicability of removing unwanted organic materials in water. The results of batch-wise processes were very good and even better for continuous systems. The aim of this thesis was to study the process in a continuous stirred tank reactor, to gather data which would be useful in studying the phenol oxidation mechanism, and to see if the use of a mechanically agitated reactor can be justified. Also the study was to gather data on the reactor gas holdup ratio, an important factor for a reactor of this kind.

EXPERIMENTAL

1. Pilot Plant

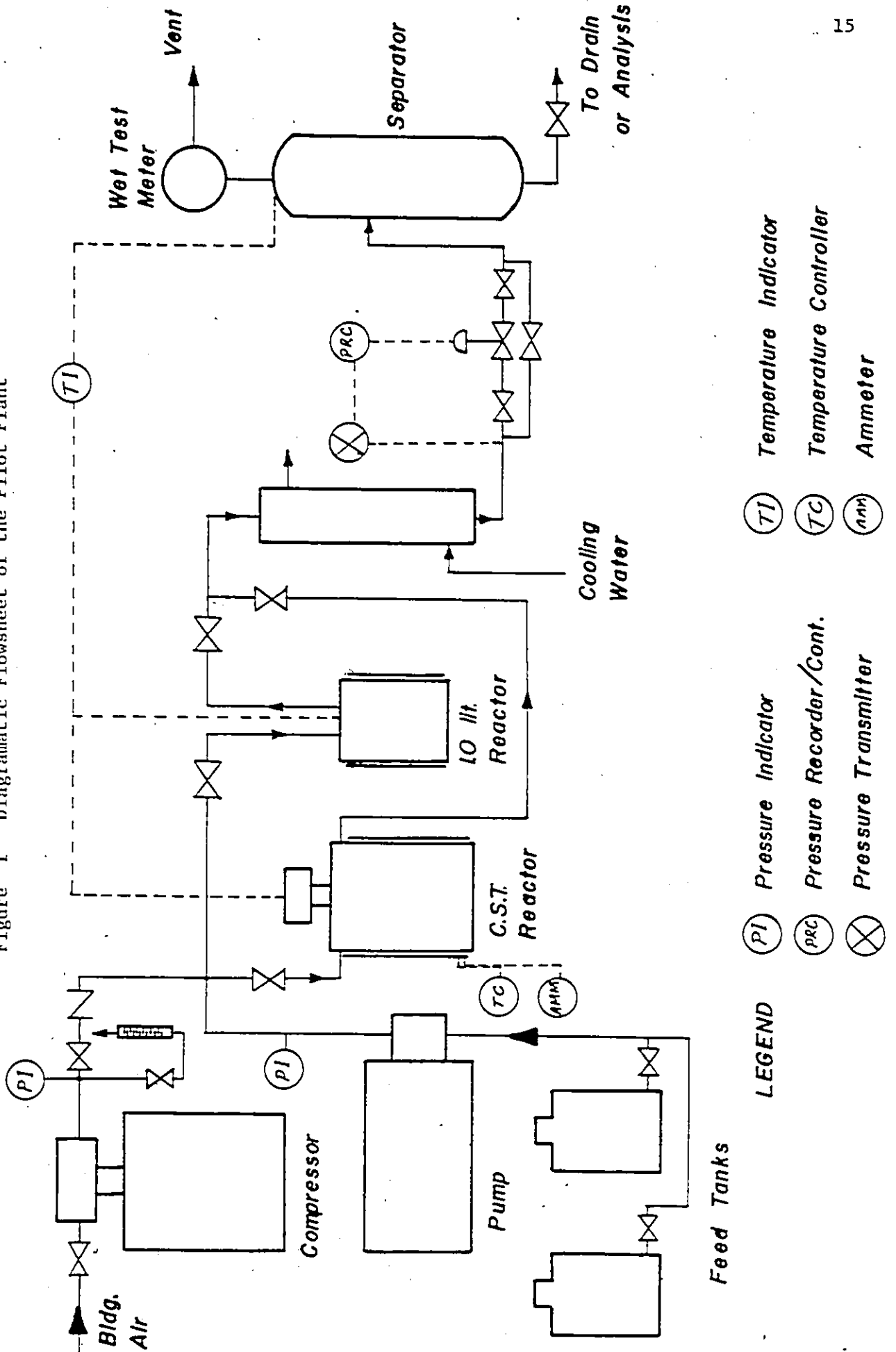
The design of the pilot plant used in this investigation was based on Zimmermann's papers with some modifications (mostly on the preheat heat exchangers) to simplify the operation. A diagrammatic flowsheet of the plant is shown in Figure 1 .

Two feed tanks were used. One for distilled water which was a 13 U.S. gallon polyethylene bottle with spigot, number B7586-13, supplied by Canadian Laboratory Supplies Limited. The other tank was used for phenol solutions, a polyethylene cylindrical tank, model S9110-60 with 30 Imp. gallon capacity, equipped with a floating polyethylene tank cover model S9110-54C, supplied by Canadian Laboratory Supplies Limited.

All process tubings, fittings, and valves were 1/4" low pressure (LP) 316 stainless steel supplied by Pressure Products Industries, Hatboro, Pennsylvania.

The liquid feed pump was a diaphragm-type, positive displacement machine, model CP-3 "Pulsafeeder", supplied by Interpace Corporation, Lapp. Insulation Division, Le Roy, New York. Pump capacity was 0.85 to 242 U.S. gallon per hour. The maximum output pressure was 5,000 psig. Desired flow rates were obtained by adjusting the piston stroke length.

Figure 1 Diagrammatic Flowsheet of the Pilot Plant



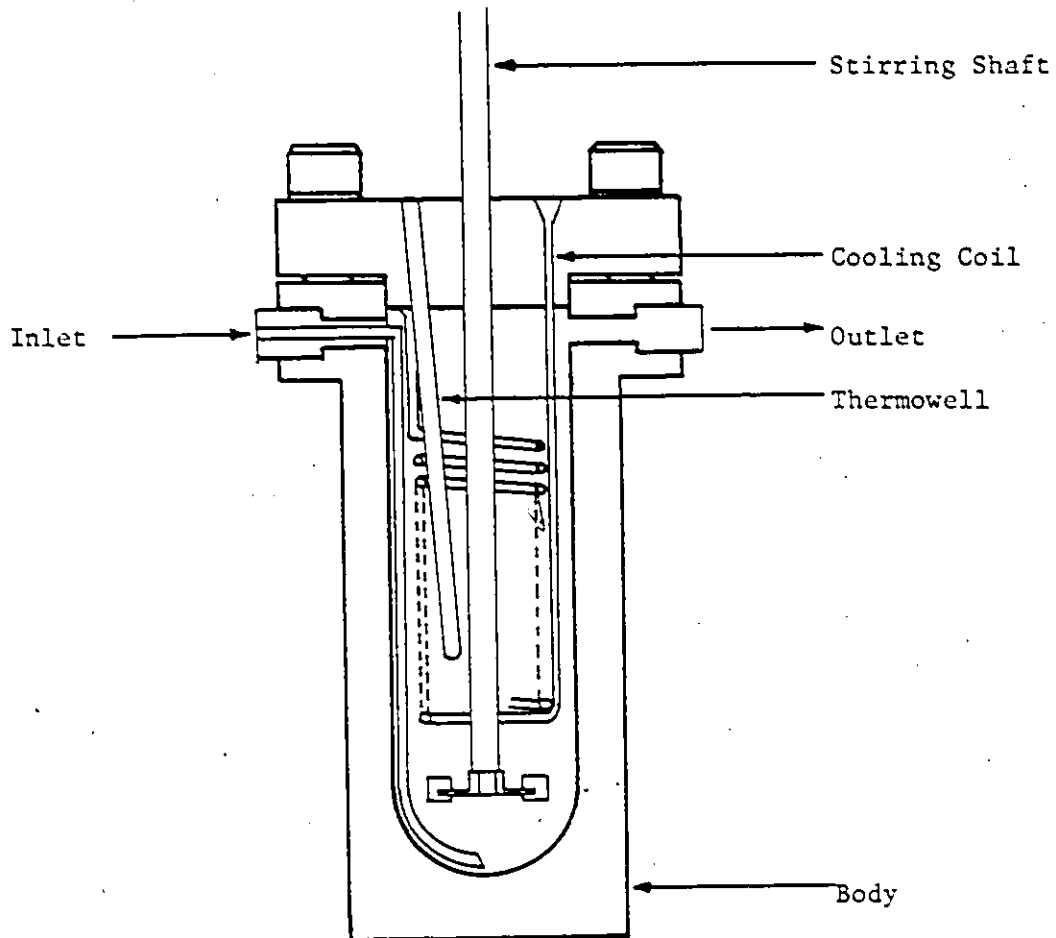
- LEGEND
- (PI) Pressure Indicator
 - (TC) Temperature Controller
 - (AMM) Ammeter
 - (T/I) Temperature Indicator
 - (PRC) Pressure Recorder/Cont.
 - (X) Pressure Transmitter

The air was fed to the system by an air compressor. This was a diaphragm type, reciprocating, two-stage compressor, model Q-071038 supplied by Pressure Products Industries. The compressor's maximum output capacity was 125 standard ft³/hour at 5,000 psig discharge pressure. The excess air were bled off and the desired air flow rates to the system were regulated by a needle valve and a rotameter in the discharge line. The rotameter was a Brooks, tube size R-6-15-B, with a stainless steel float.

Discharge pressures of the air compressor and liquid pump were monitored by two identical pressure gauges, model W-5-1, "ASTRAGUAGE", supplied by Pressure Products Industries.

The reactor was a model SMS, "AGITATED REACTOR", supplied by Pressure Products Industries. It was a stainless steel cylinder of one U.S. gallon capacity equipped with a gaspersator type six-blade agitator, an electrically driven motor, a rupture disc assembly, one inlet line reaching the bottom of the reactor, and four outlets supplied on the body. A thermowell and a cooling coil were also installed on the reactor cover. Figure (2) shows an inside view of the reactor.

The reactor was heated by nine electrical strip heaters arranged in three parallel circuits each containing three heaters in series. The strip heaters were model SE-1405, 500 watts, supplied by Canadian Chromalox Limited, Toronto, Ontario. They were installed on the outside surface of the reactor wall and covered with a layer of asbestos paper then 2 1/2" of glass wool.



Inside diameter = 5 inches
 Inside length = 12 inches
 Inside volume of reactor = 3,898 cm³
 Cooler tube volume +
 Thermowell volume +
 Stirring shaft volume = 250 cm³
 $V_R = 3,898 - 250 = 3,648$ cm³

Figure 2 Inside View of the Reactor

A tube-and-shell heat exchanger was used to cool down the reactor's effluents, with cold water in the shell running counter-current to the process stream. The shell was a piece of 4 1/4" O.D., 22" long. Copper pipe and the tube was made of 22" long low pressure stainless steel tubing. The heat exchanger was manufactured by the Department Machine Shop.

The gas-liquid separator was a cylindrical stainless steel tank, 23" high by 8" outside diameter and was built in the Department Machine Shop. It was equipped with a thermocouple to record the liquid temperature in the bottom of the separator.

A wet test meter on the exit gas line of the gas-liquid separator was used to monitor the air flow rates. The meter was of series G-3000-1 stainless steel, maximum capacity of 24 ft³/hour, supplied by Canadian Laboratory Supplies Limited.

A temperature controller by Brown Pyr-O-Vane, range 0-1400 °F, was used to control the reactor temperature and was supplied by Honeywell Controls Limited. Control was indirect i.e., the outside reactor skin temperature was controlled to furnish the reactor with desired inside temperature.

The reactor inside temperature was recorded by an Electronik 16 Multiple-point Strip Chart Recorder, supplied by Honeywell Controls Limited. This temperature recorder/indicator could record up to 12 temperatures and had a range of 0-400 °C.

The pressure control system was a standard three-part system supplied by Honeywell Controls Limited. The pressure transmitter

was a non-indicating type, model 738-N1H3, range 0-4000 psig. The pressure recorder was a model 51311 with an integrally mounted two-mode controller, model 52201. The pressure control valve was a 1/4 inch "Research Control Valve".

The instrument air was supplied from the building supply air line and was filtered through an Instrument-Air Filter, part no. 2306, supplied by Moor Products Company.

The balance which was used for weighing the phenol crystals and the chromatograms was a type 416, no. 140015, by E. Mettler supplied by Fisher Scientific, with ± 0.0005 gm accuracy and a maximum load of 80 grams.

A hand pump was used for pressure testing and leak detection after the plant was assembled. This was a model OH-100-15, supplied by Pressure Products Industries.

The phenol was purchased in crystal form as "Baker Analysed Reagent" grade from Canadian Laboratory Supplies Limited.

Distilled water from a laboratory still was used in preparation of all feed solutions.

The air intake of the compressor was supplied from the building supply air line and was filtered before feeding the compressor at 35 psig. The air filter was the same used for filtering instrument air.

2. Plant Assembly and Calibration of Equipments

The task of assembling the plant was straightforward as some of the components were available from a study of the same kind using a non-mechanically agitated reactor. The system was pressure tested before the start-up to check for proper installation and for any possible leaks. This was done by means of the previously described liquid hand pump using water at a pressure of just under 5,000 psig. This testing pressure was selected because the reactor rupture disc assembly would burst at pressures over 5,000 psig. The system was pressure tested whenever the reactor seal was replaced.

The compressor and the rotameter calibration data were supplied by the manufacturers. Air flow rates were double checked with the wet test meter.

The liquid feed pump was calibrated at various discharge pressures. The pressure gauges were checked at various pressures, giving identical readings on all three gauges while the system was being pressure tested.

The temperature indicator/recorder was calibrated by means of a potentiometer and this was repeated several times in course of experiments.

The calibration of the chromatograph is demonstrated in detail in the Appendix.

3. Analysis

There are two methods available for the analysis of phenol in water solutions. One is Method D-1783-70 of ASTM Standards²⁵ that involves the distillation of sample followed by colorimetric analysis using a spectrophotometer. This method is very time-consuming but also is the only method that can be used for very low phenol concentrations as well as for higher concentrations.

The other method, also demonstrated by ASTM Standards, Method D-2580-68,²⁵ employs gas-liquid chromatography. This method is much simpler to perform and enjoys the same degree of accuracy as the previous method once the injection technique has been mastered. Wider concentration range of phenol solutions can be used in this method. It was decided to use this method for detecting phenol concentration in all of the experiments the details of which is given in the Appendix.

Phenol analysis were performed using a "Varian Aerogram" model 1400 chromatograph. The column was a 1/8" by 10' stainless steel tube, packed with 60/80 mesh Chromosorb W (acid washed) coated with 5% weight Free Fatty Acids. The detector was a flame ionization type. The chromatograph was coupled to a recorder of the type "Honeywell Electronic 194 Laboratory Recorder". The calibration of chromatographic column was done by known phenol concentrations and the Standardization Value thus obtained was used to find unknown phenol concentrations. The details of such calculations are presented in the Appendix. For each run three samples of feed and four or

more samples of the effluent were taken. Each sample was analyzed three times using the chromatograph.

Analysis on diphenyl ether was performed on the above chromatograph using the same technique.

Concentration of acetic acid solutions were measured on the same chromatograms by comparing the peak area to the ones for pure acetic acid samples of known concentrations.

Analysis was also made to find the degree of saturation of the vapor phase in the reactor. The detail of these experiments are given in the Appendix.

4. Procedure

I- Gas Holdup Analysis

A typical run to study the gas holdup ratio proceeded as follows:

1. Feed tank was filled with distilled water.
2. The liquid pump was started to feed the reactor with desired flow rate. This was done by pre-adjusting the pump setting.
3. Cooling water was started to circulate in the heat exchanger.
4. The air compressor was started and was kept isolated from the system by discharging all output air through a bleed rotameter.

5. As the desired reactor pressure had been reached (by then the reactor was almost full of water), the pressure controller was switched from "MANUAL" to "AUTOMATIC" mode.
6. The compressor discharge valve to the system was opened and the desired air flow rate was set up by adjusting the bleed rotameter.
7. The system was kept under these pre-determined conditions for about five liquid residence times.
8. After the system reached to steady-state operation, the reactor was isolated from process lines at once. The gas holdup was then obtained by measuring the amount of water remaining in the reactor. This water volume was measured by a graduated cylinder at room temperature as the reactor content was taken out and cooled in the heat exchanger. The water volume thus obtained was corrected for reactor conditions assuming the vapor phase in the reactor was saturated. This assumption is based on the results of an investigation over the reactor gas phase the results of which are presented in the Appendix.
9. The reactor temperature was set at 200 °C at all times when the system was not operating. This was done to prevent any leakage from the Teflon-O-Ring due to heating-cooling effects on the reactor.

II- Wet Air Oxidation Experiments

The necessary data was obtained by adopting the following operating procedure of the pilot plant.

1. A desired amount of phenol crystals was weighed on the balance and dissolved in distilled water to prepare a desired phenol solution.
2. Two feed tanks, one filled with distilled water and the other with phenol solution of desired concentration were prepared. The samples of phenol solution were also taken.
3. The liquid feed pump was adjusted to the desired feed rate and initially started with distilled water as feed. This was done to prevent possible tar formations as the initial feed to the reactor was vaporized. The procedure steps 3, 4, 5 and 6 of gas holdup analysis were then followed.
4. The liquid feed pump was switched to phenol solution and the system was operated until the desired temperature and pressure was reached.
5. The system was kept under these conditions for about five liquid residence times and the outlet samples were taken during an additional two or three liquid residence times thereafter.
6. The liquid pump was switched to distilled water to wash out all the phenol remained in the reactor.

7. The liquid pump was switched off and the air compressor was isolated from the system. Pressure controller was set at zero and the bypass valve was opened to let the reactor be depressurized.
8. The air compressor was allowed to run idle for 15 minutes before it was switched off. All other elements except the temperature control device and strip heaters were turned off.

RESULTS

1. Gas Holdup Ratio Study Results

This study was done to produce more reliable figures for liquid residence times in the reactor.

To study the effect of each process variable on gas holdup, all other variables were kept constant. Thus the effects of temperature, pressure, and gas and liquid flow rates as well as agitation speed were studied.

The experimental data gathered for this study are tabulated in Table (2) of the Appendix. There were some restrictions on the range of process variables such as the air flow rate which was restricted because of control valve capacity. That made it impractical to operate at high gas flow rates and low pressures, as there was still pressure built-up while the control valve was in "Fully-open" position.

Effect of Liquid Flow Rate

The results show that beyond the rate of 4,000 ml/hr. there was little change in gas holdup and it practically remained unchanged for higher liquid flow rates as can be seen from Figure 3. It also shows that gas holdup increased rather sharply at liquid flow rates less than 2,000 ml/hr. and can be expected to be 100% at a liquid flow rate of zero.

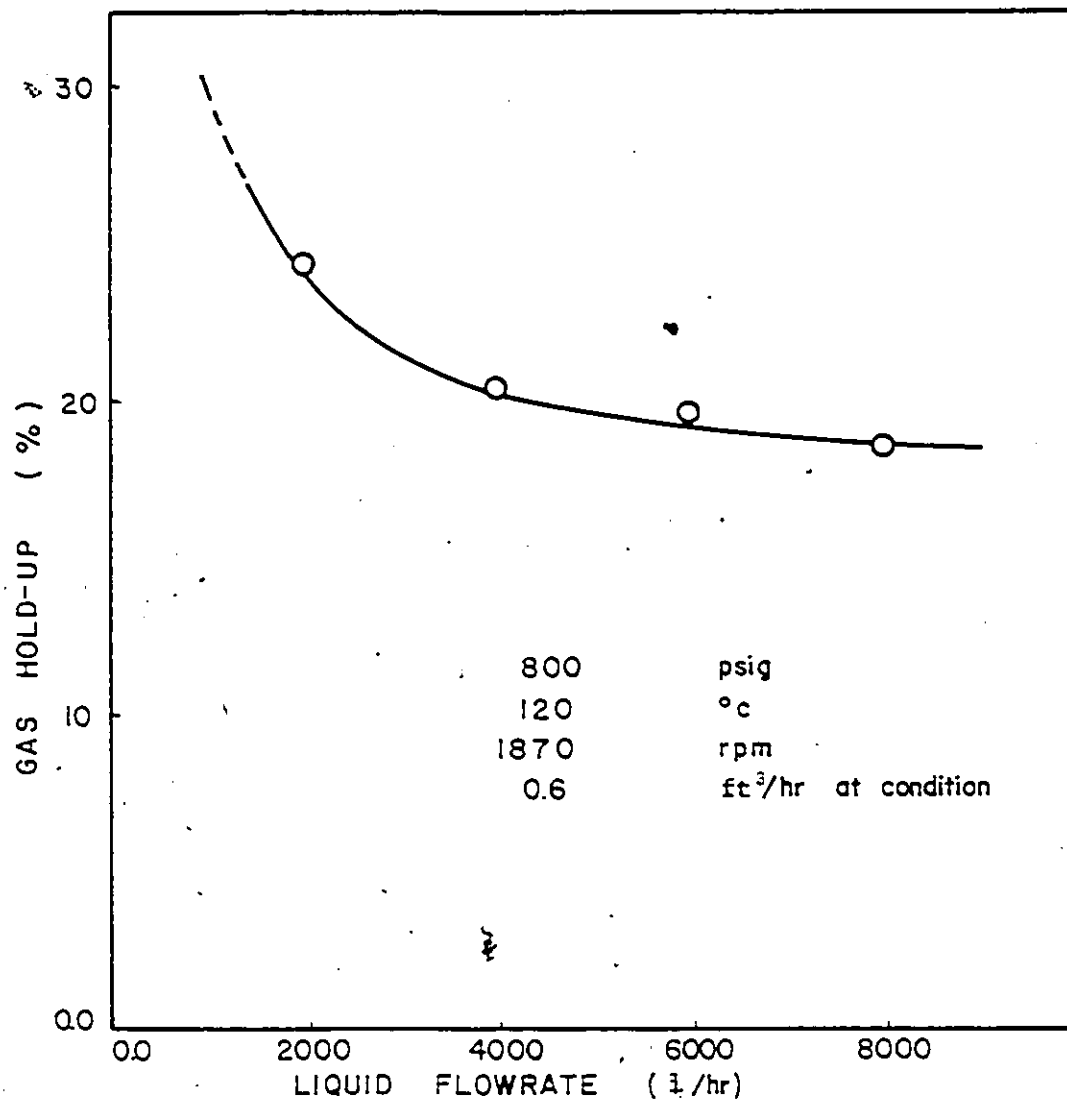


Figure 3 Gas Holdup vs. Liquid Flow Rate

Effect of Air Flow Rate

As is shown in Figure 4, the holdup increased very sharply with increased air flow rate and then remained constant for air flow rates over 0.15 ft³/hr. at reactor conditions of 120 °C and 800 psig. The gas holdup is theoretically expected to be zero percent at zero gas flow rate.

Effect of Temperature

Within the range of study it seemed from Figure 5 that the gas holdup did not change considerably with respect to temperature. This however may not be generalized as the gas holdup depends on such liquid characteristics as vapor pressure, viscosity, surface tension, and density. Consequently the temperature dependency of gas holdup would be a complex function of many such factors and Figure 5 only can show the overall effect of temperature on these factors for an air-water system and only within the range of study.

The gas holdup ratio for air-water system is expected to be 100% for temperatures over 374.1 °C, the critical temperature of water. In a more precise determination of this effect, similar studies at other pressures with more data points would be needed.

Effect of Pressure

It can be seen from Figure 6 that the gas holdup tended to remain unchanged as the pressure was increased over the wide range

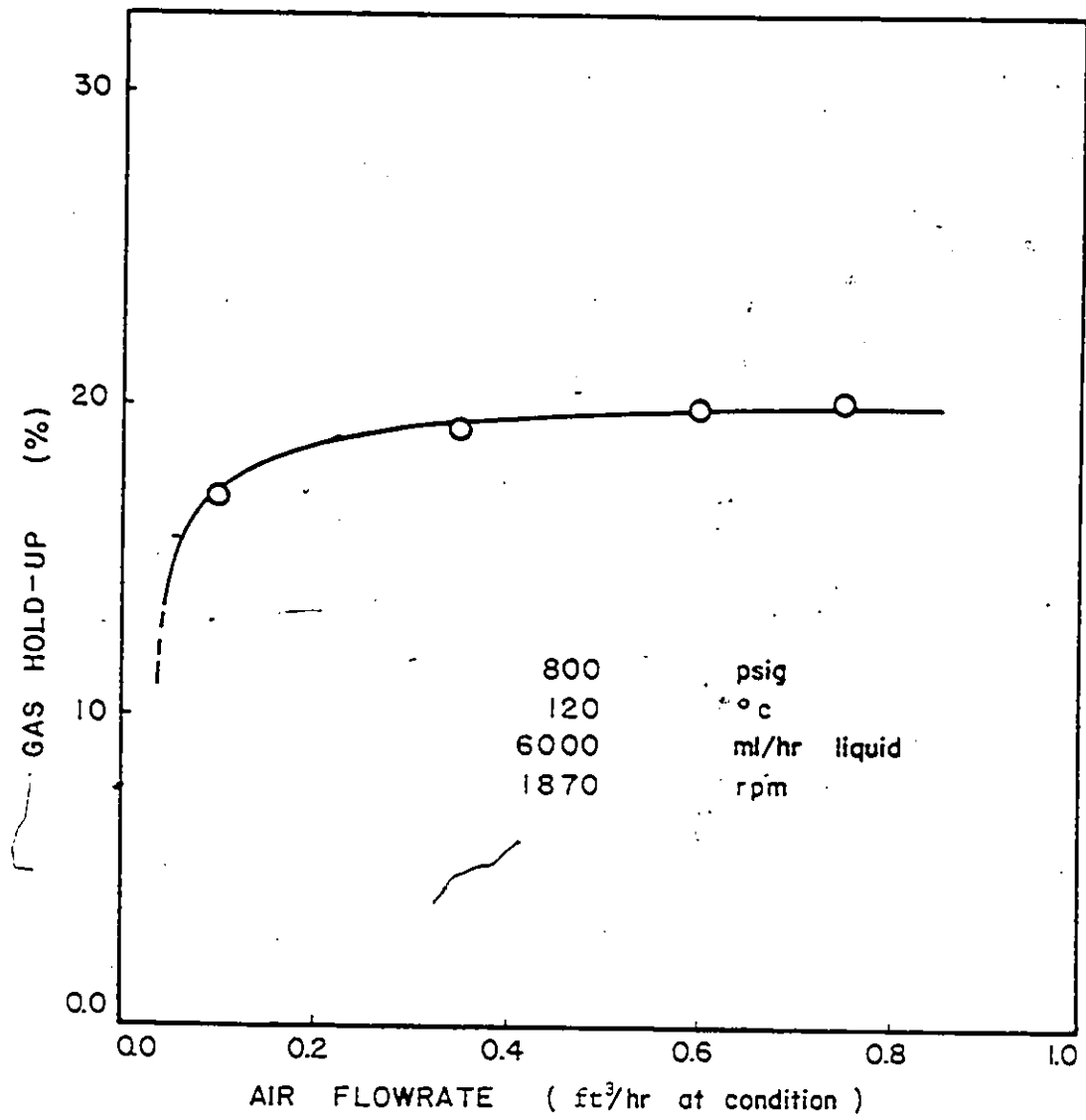


Figure 4 Gas Holdup vs. Air Flow Rate

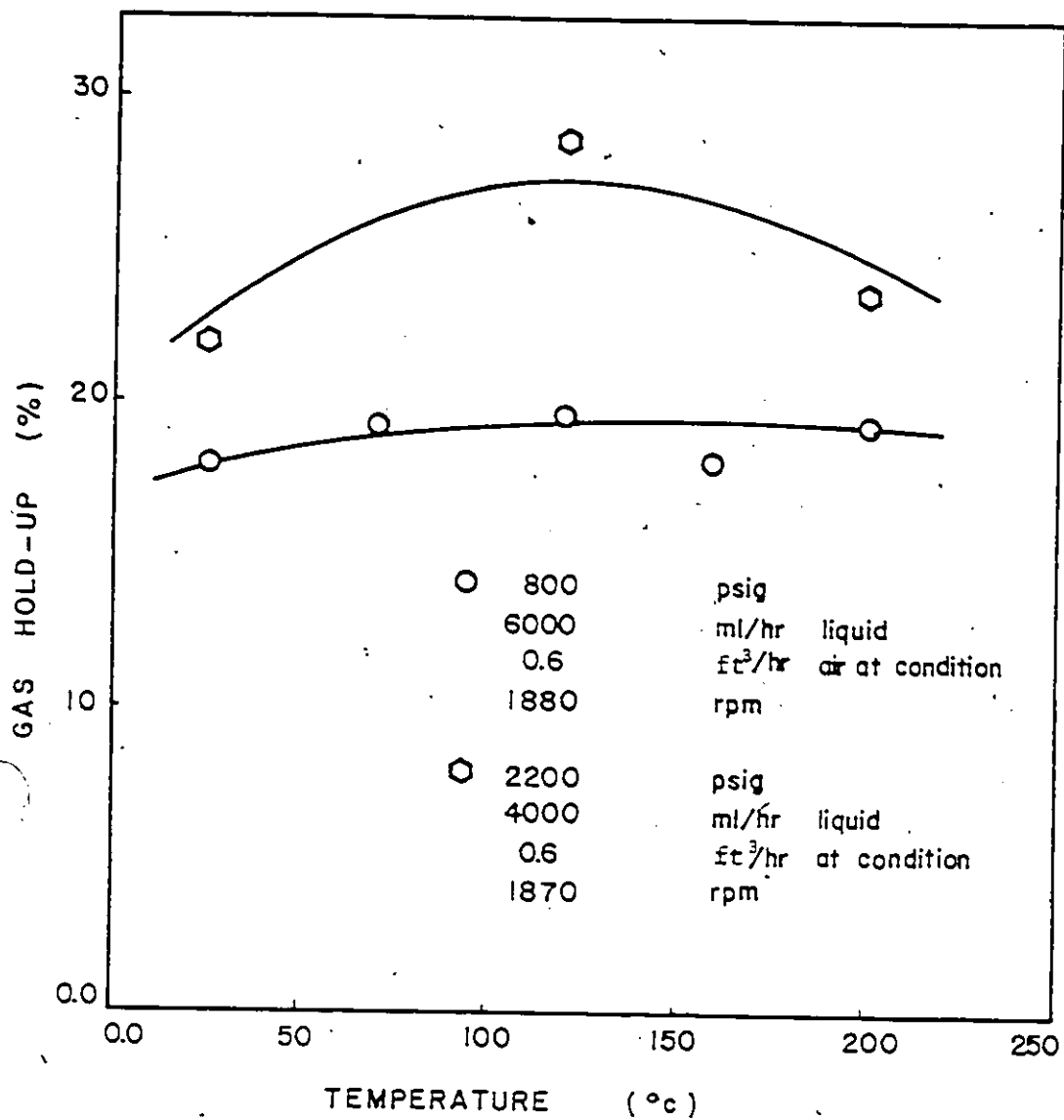


Figure 5 Gas Holdup vs. Temperature

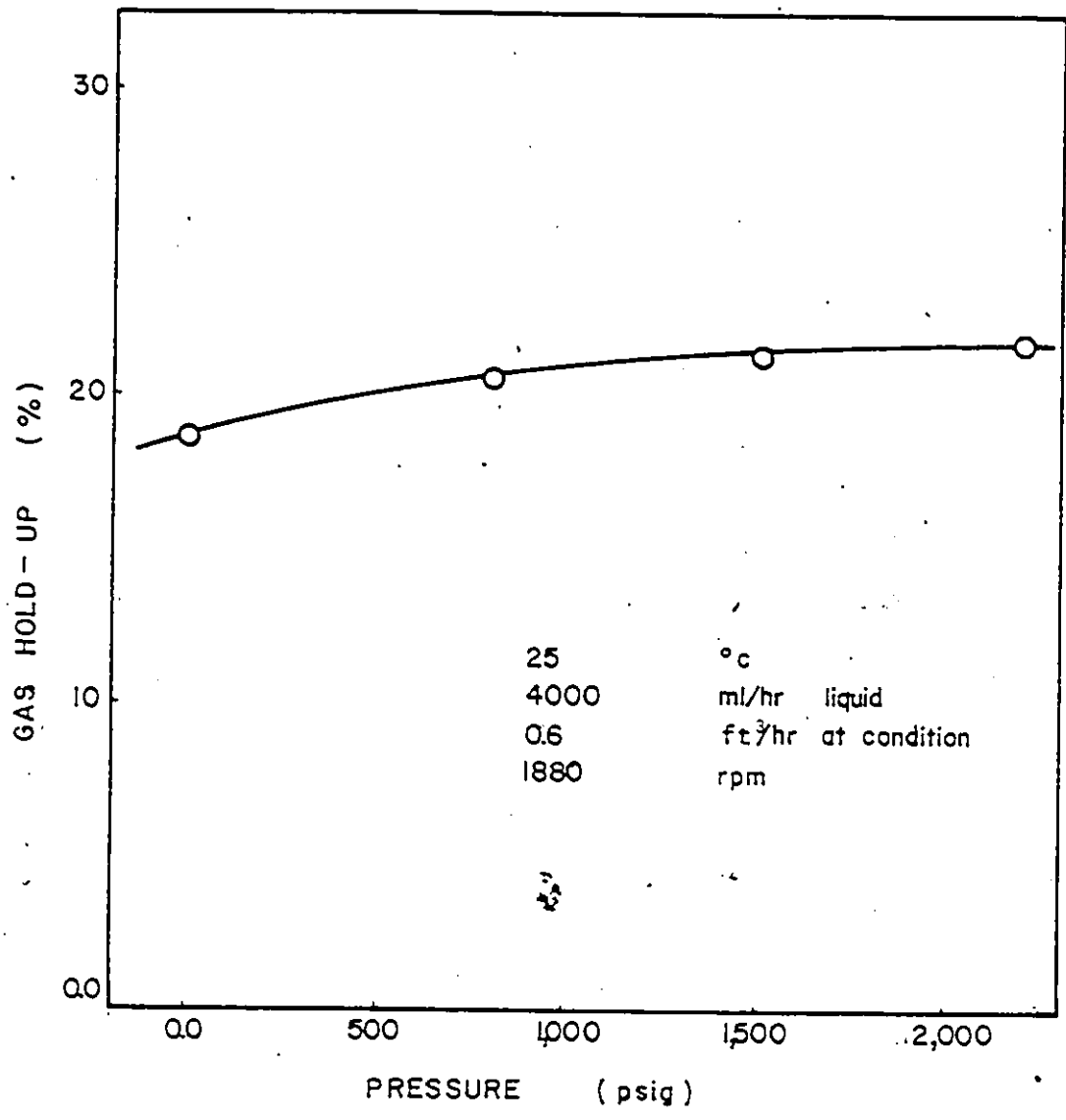


Figure 6 Gas Holdup vs. Reactor Pressure

of 0.0 to 2,200 psig. This can be explained by the fact that the air flow rates were kept constant at 0.6 ft³/hr. at reactor conditions, and other factors such as the liquid properties are not very pressure sensitive.

Effect of Mixing

Figure 7 can be used to show the effect of agitation speed on gas holdup. It shows that for agitation speeds below 500 r.p.m. there was no considerable change in gas holdup. Between 800 and 1,500 r.p.m., the gas holdup increased and became constant again for agitation speeds of more than 1,500 r.p.m. where it remained insensitive to further increases of agitation* speeds.

Based on the above obtained results and the range of operating conditions used in WAO of phenol in this work were:

| | | |
|------------------|-----------|----------------------|
| Air flow rate | 0.6 | ft ³ /hr. |
| Liquid flow rate | 2000-8000 | ml/hr. |
| Pressure | 800-2200 | psig |
| Temperature | 200-250 | °C |
| Agitation speed | 1800 | r.p.m. |

the gas holdup can be assumed to be 20% for all phenol runs without much approximation.

* Different agitation speeds were obtained by means of a constant speed electrically driven motor and different pulley sizes.

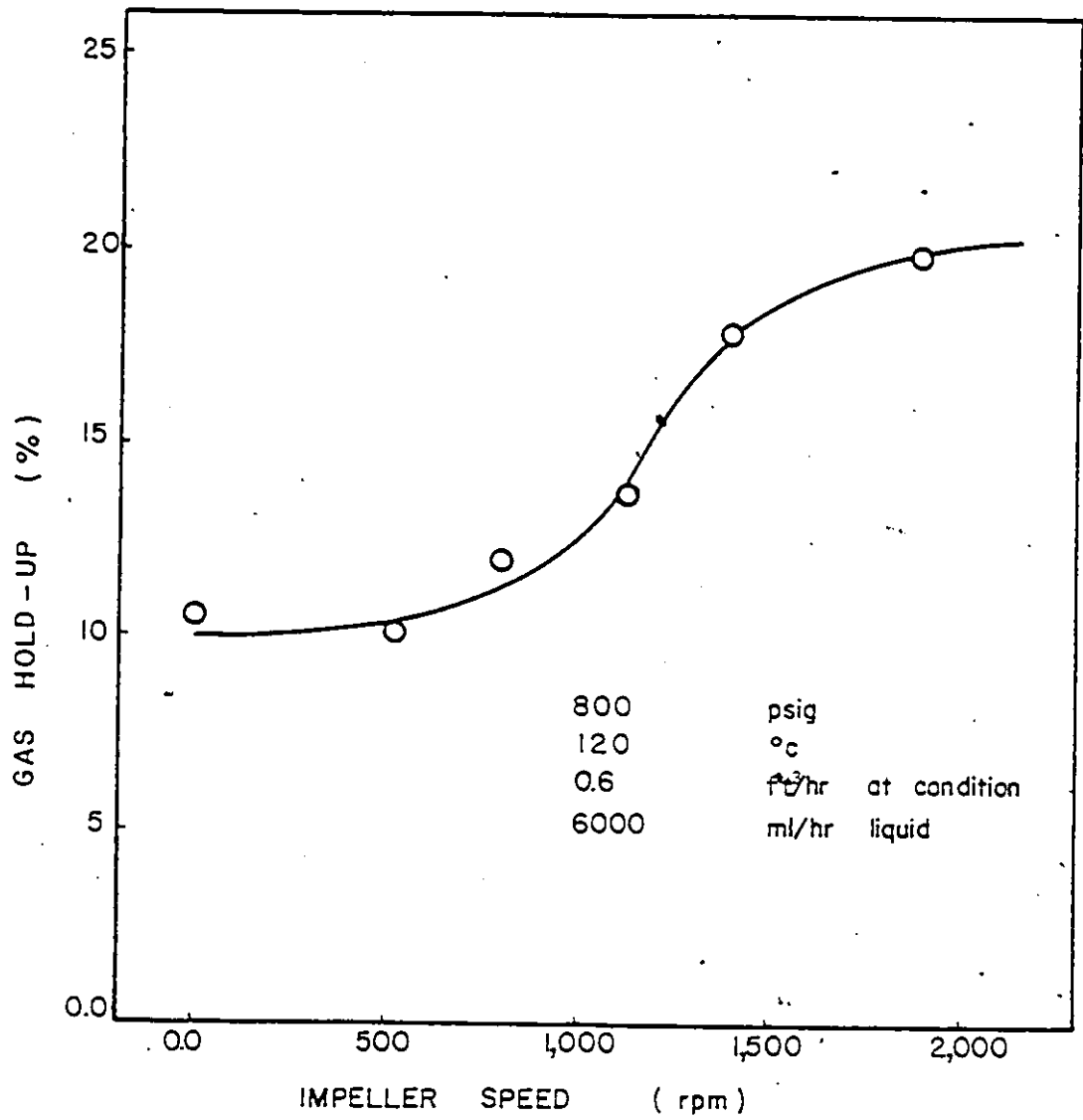


Figure 7 Gas Holdup vs. Agitation Speed

2. WAO Study Results

The scope of this project was to study the factors in the reaction control mechanism of the oxidation of phenol in aqueous solutions under mechanical agitation at elevated temperature and pressure conditions.

In this study it was decided to eliminate one variable, air flow rate, and thus a constant air flow rate of $0.6 \text{ ft}^3/\text{hr.}$ at reactor conditions was set for all experimental runs. This flow rate supplied the reactor with excess air for all runs and yet was less than the amount needed for depleting the liquid water in the reactor.

The details of all experimental runs are given in the Appendix Tables 3, 4, 5 and 6. Figures 8 to 15 are based on these tabulations.

The first four runs were blank runs with no air present. These runs at different pressures, temperatures and agitation speeds showed that there was no phenol disappearance without air being present. The results of these runs are listed on Table 3 of the Appendix.

In the next set of experiments the WAO of phenol was tried at temperatures around room temperature and to see if the Schulze and Hasse¹⁴ claim of such a reaction can be justified. The results which are listed on Table 3 of the Appendix showed that there was not any apparent reaction. This part was done under pressures of 0.0, 800, 1,500 and 2,200 psig., concentration of 1,000 mg/l. and

liquid residence times of 0.6 and 0.7 hr., with agitation speed of 1,800 r.p.m., where no measurable change in the phenol concentration was noticed.

The temperature was raised to 120 °C for the next set of experiments. The results are listed on Table 4 and showed that again the reaction would not proceed at this temperature. The experiments were done at three different pressures (800, 1,500 and 2,200 psig.) with feed concentrations of 1,000 and 4,000 mg/l., liquid residence time of 0.36 hr., and agitation speed of 1,800 r.p.m.

Figures 8, 9, 10 and 11 show the change in phenol conversion with respect to reactor total pressure for several runs at temperature of 200 °C. Considering these figures it can be seen that high degrees of conversion of phenol were achieved in the application of WAO process at this temperature.

The effect of liquid residence time on phenol conversion at 200 °C and different pressures can be seen in Figure 12. This figure was also employed to predict the conversions for residence time of 0.36 hr. The conversion values were then corrected for feed concentration and the results are shown in Figure 13. This figure shows the change in phenol conversion versus the reactor total pressure at 200 °C with feed concentration of 4,450 mg/l. and liquid residence time of 0.36 hr.

Figure 14 is an equivalent curve for runs at 250 °C. The effect of temperature could be studied considering Figures 13 and 14.

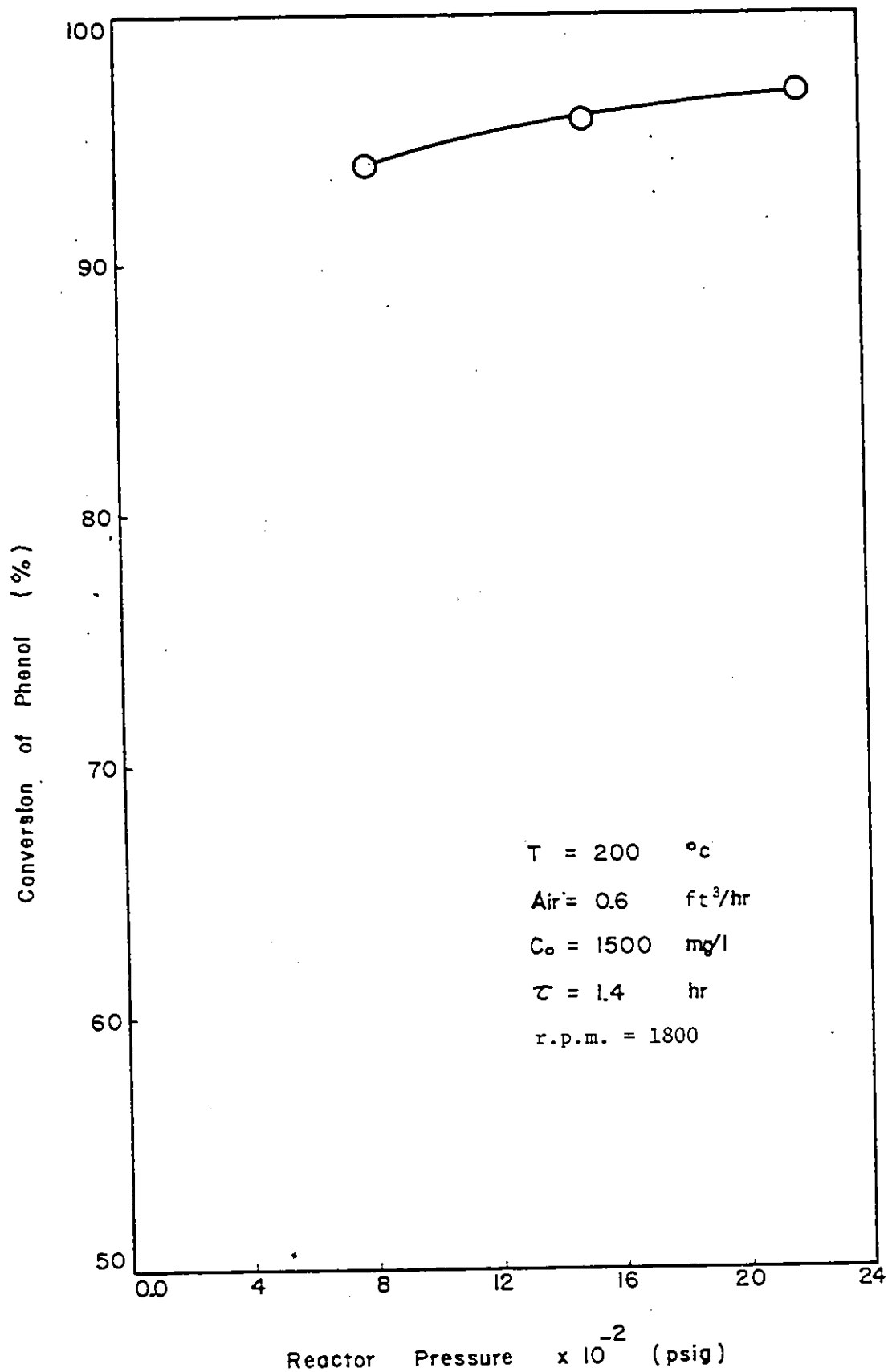


Figure 8 Phenol Conversion vs. Reactor Pressure at $200 \text{ } ^\circ\text{C}$ with $C_{\text{Ph}(0)} = 1500 \text{ mg/l}$, $\tau = 1.4 \text{ hr}$

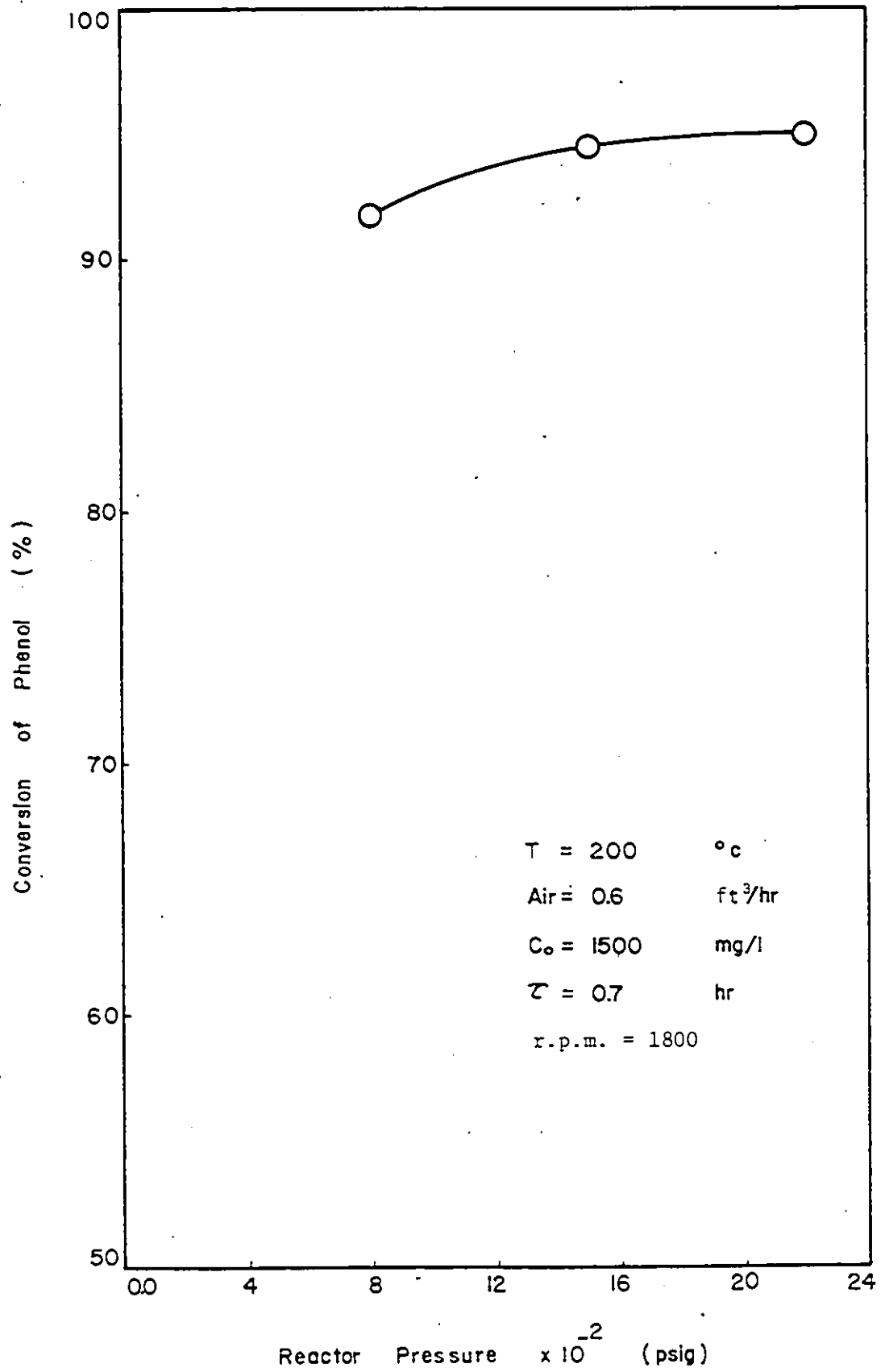


Figure 9 Phenol Conversion vs. Reactor Pressure at 200 °C with $C_{Ph(0)} = 1500$ mg/l, $\tau = 0.7$ hr

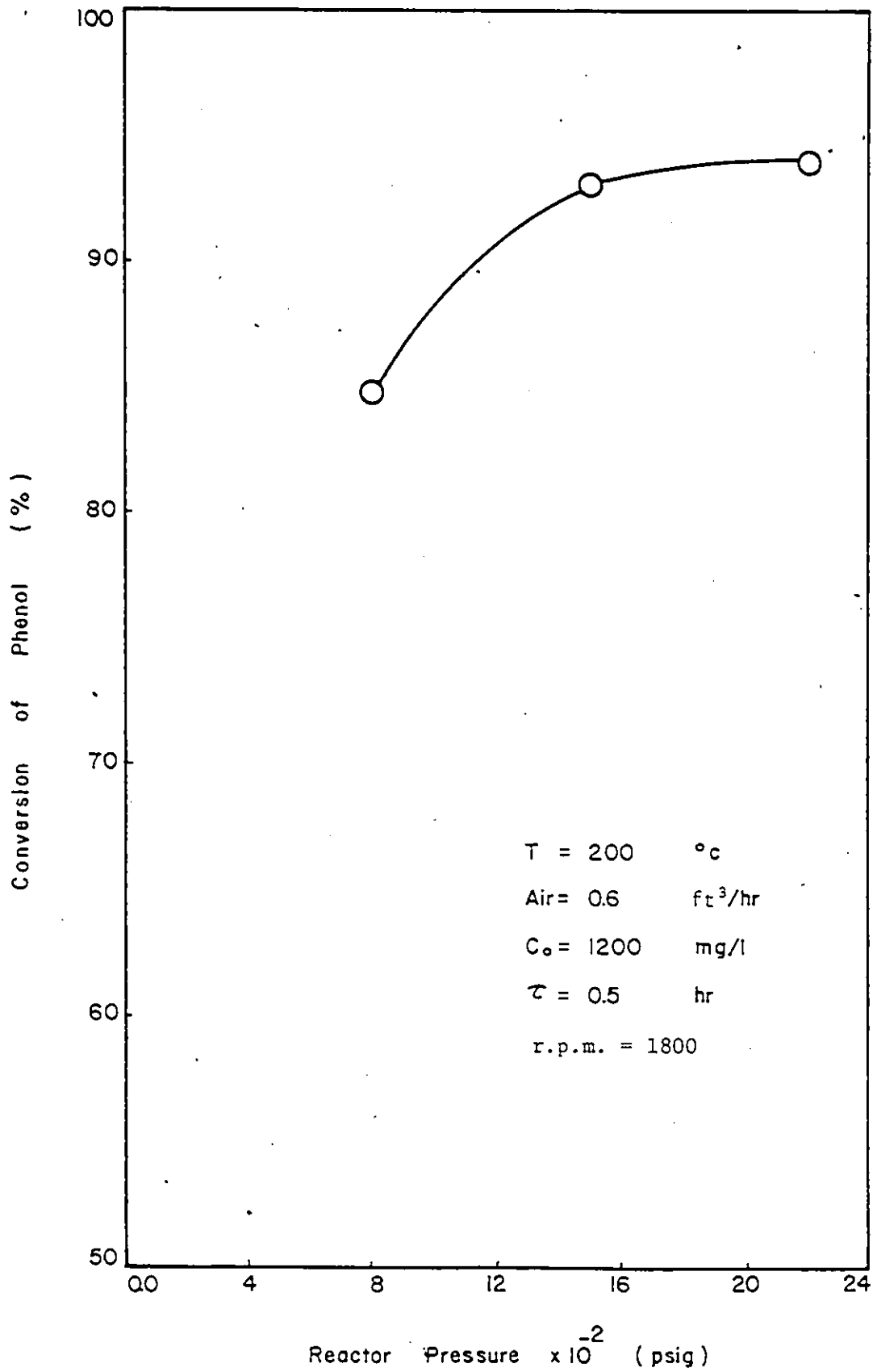


Figure 10 Phenol Conversion vs. Reactor Pressure at $200 \text{ } ^\circ\text{C}$ with $C_{\text{Ph}(0)} = 1200 \text{ mg/l}$, $\tau = 0.5 \text{ hr}$

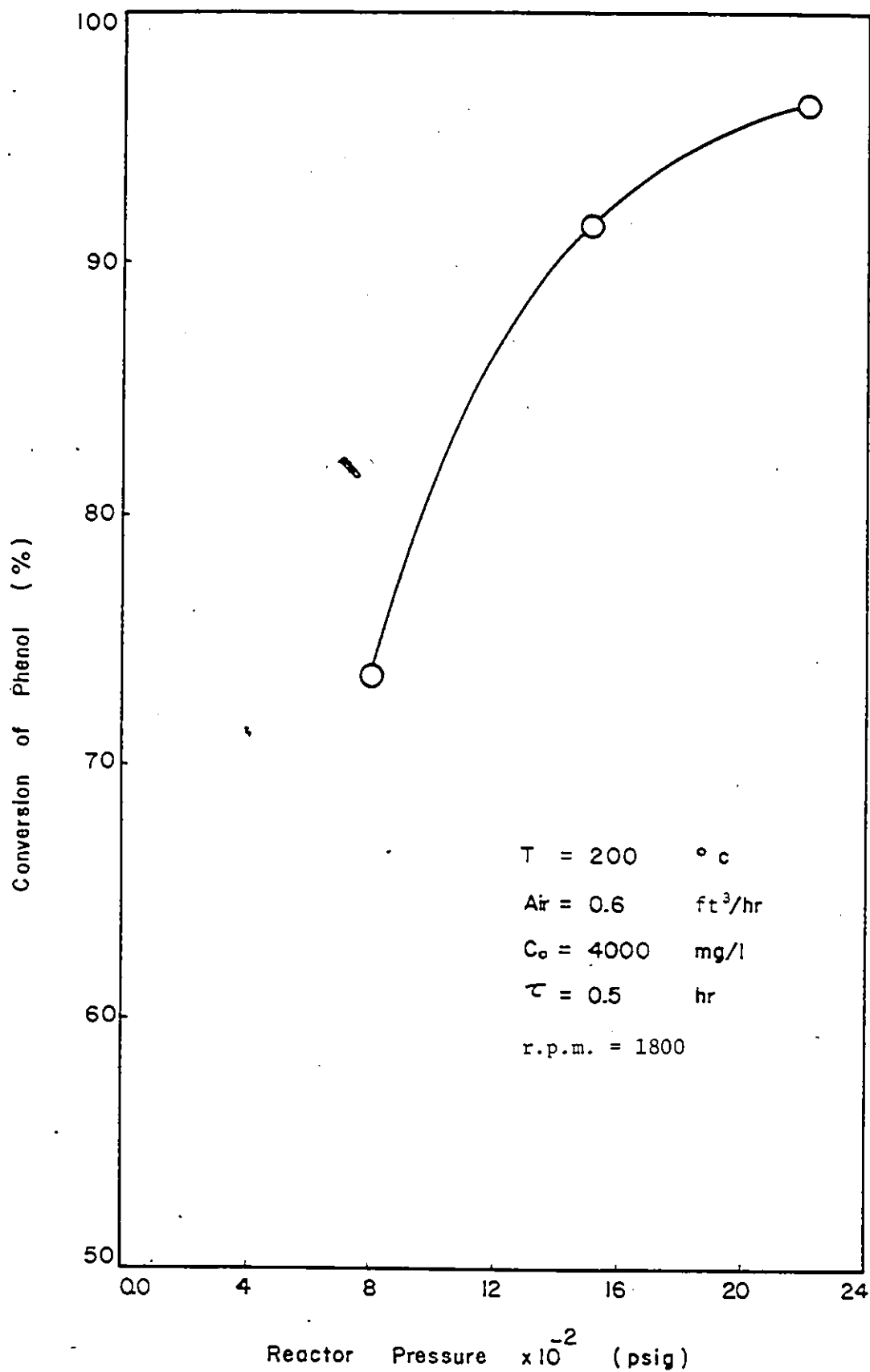


Figure 11 Phenol Conversion vs. Reactor Pressure at 200 °C with $C_{\text{Ph}(0)} = 4000 \text{ mg/l}$, $\tau = 0.5 \text{ hr}$

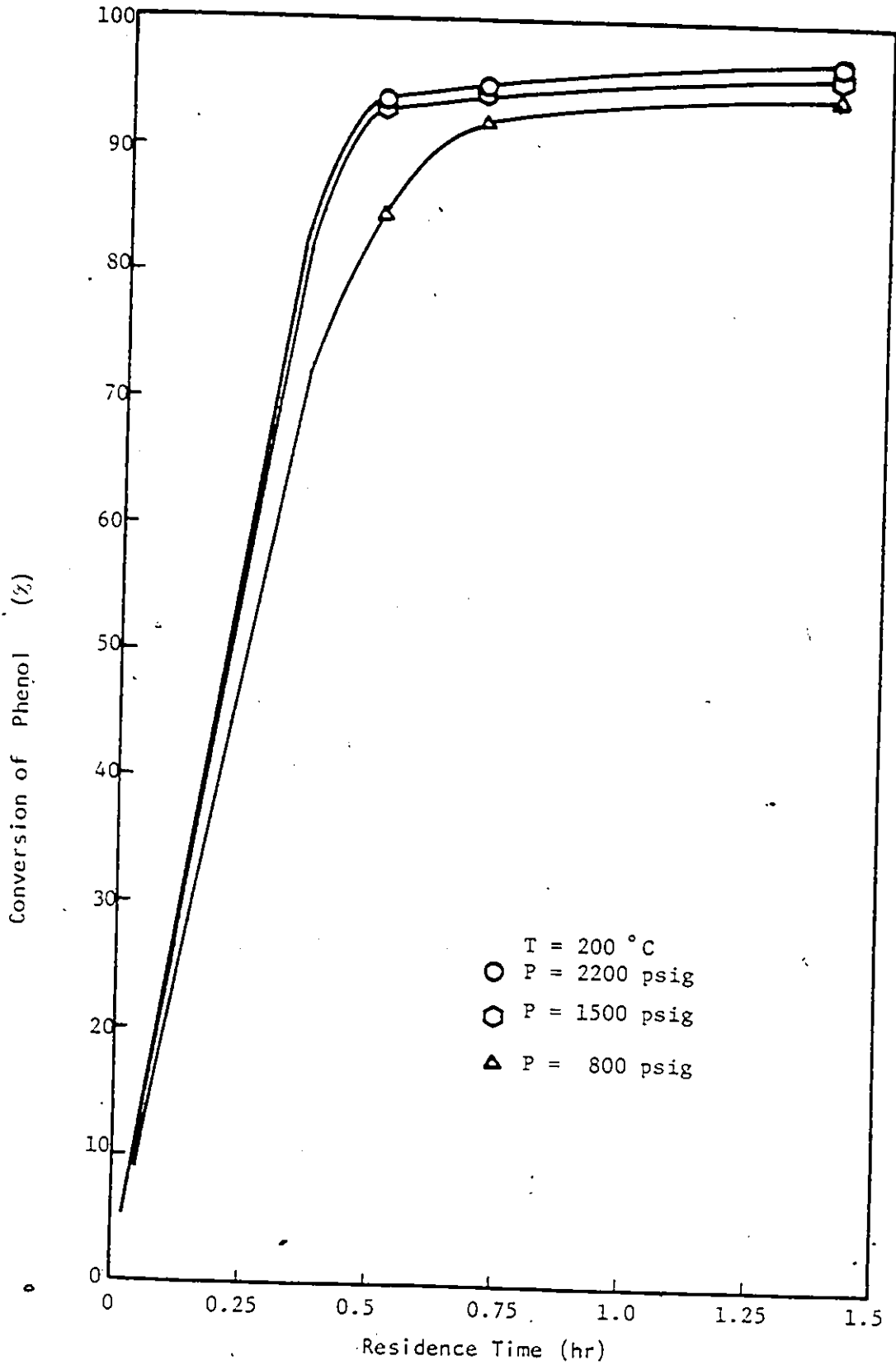


Figure 12 Phenol Conversion vs. Liquid Residence Time at 200 °C and pressures of 800, 1500, and 2200 psig

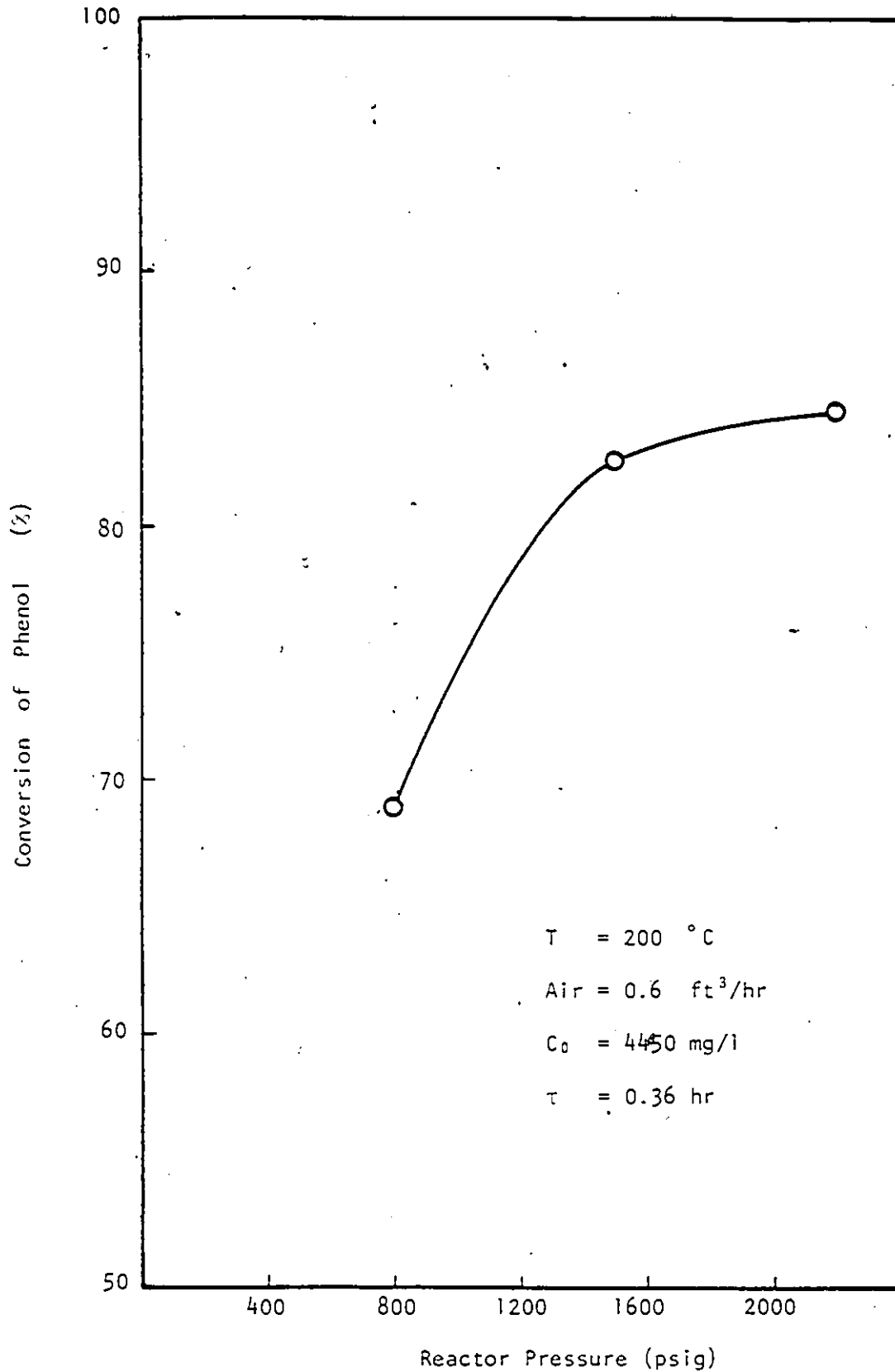


Figure 13 Phenol Conversion vs. Reactor Pressure at $200 \text{ }^\circ\text{C}$ with $C_{\text{Ph}(0)} = 4450 \text{ mg/l}$ and $\tau = 0.36 \text{ hr}$

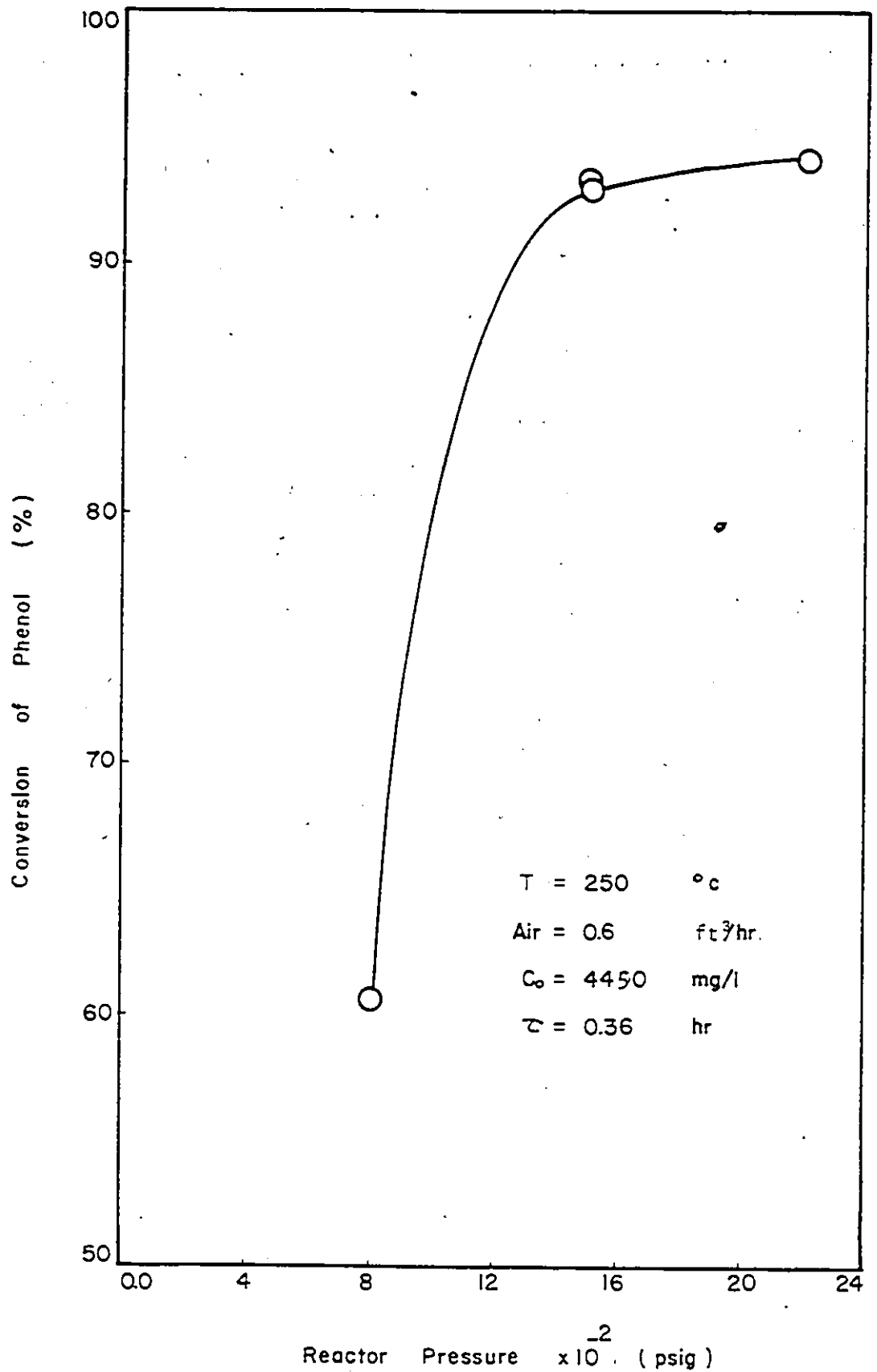


Figure 14 Phenol Conversion vs. Reactor Pressure at $250 \text{ } ^\circ\text{C}$ with $C_{\text{Ph}(0)} = 4450 \text{ mg/l}$ and $\tau = 0.36 \text{ hr}$

Figure 15 compares the phenol conversions at 200 and 250 °C. In this figure conversions are plotted versus the partial pressure of oxygen in the reactor and not the total reactor pressure to show temperature effects more adequately as will be discussed in the next chapter.

It was assumed previously by Ferguson¹³ that the gas phase in the reactor was saturated. An experimental investigation was made in this study that confirmed this assumption. The results of these experiments are presented in the Appendix.

3. Determination of the Operating Conditions of WAO

Once the rate of the liquid to be treated, the amount of material in the liquid to be oxidized, and the degree of conversion desired are known, the operating conditions of WAO could be selected as followings:

1. Temperature (T): Based on the results of the experiments, there was a lower level of temperature below which the reaction did not proceed for phenol oxidation. This temperature between 120 and 200 °C, can be assumed to be 150 °C based on Zimmermann's²⁶ studies on various organic feed solutions. Furthermore, as there existed a temperature beyond which water in the liquid phase would cease to exist (critical temperature of water, 370 °C) and whereas the presence of liquid water is a vital asset in WAO, then the upper limit of operating temperature is less than 370 °C and thus $150\text{ °C} < T < 370\text{ °C}$.

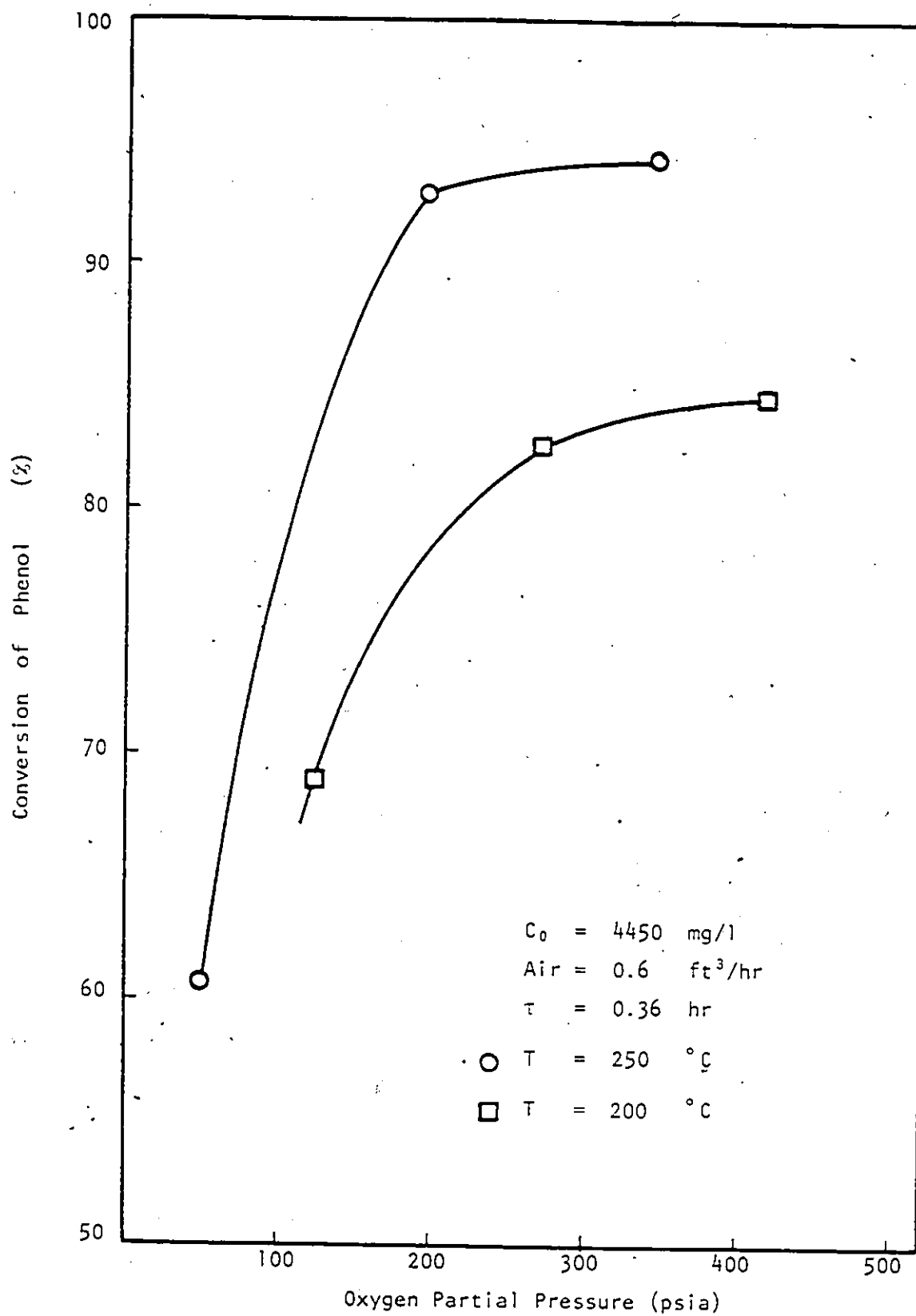


Figure 15 Phenol Conversion vs. Partial Pressure of Oxygen at 200, 250 °C, $\tau = 0.36 \text{ hr}$, $C_{\text{Ph}(0)} = 4450 \text{ mg/l}$

2. Reactor Pressure (P): After the temperature is selected, reactor pressure can be anywhere above the vapor pressure of water at that temperature. But also it can be seen from conversion-versus-pressure curves that conversion could not be improved by increasing the pressure beyond certain limits (nearly 2000 psig.). Thus the operating reactor pressure should be in the range of

$$p_w \text{ at } T < P < 2000 \text{ psig.}$$

3. Liquid Residence Time (τ): As is described earlier, there existed a trade-off between τ and P, thus by knowing the reactor pressure, the value of τ could be determined such that the desired degree of conversion was reached.
4. Reactor Volume (V_R): The reactor volume can be calculated based on the liquid feed rate, the gas holdup ratio, and the liquid residence time..

It can be seen that a combination of conditions for the operating variables exists and this adds to the flexibility of WAO process. The above can be used for checking the suitability of the WAO process for treating various materials. For example, where temperatures of over 370 °C are needed for the materials to be oxidized with an acceptable rate, the above shows that this can not be achieved by WAO process.

DISCUSSION

1. Theoretical Basis for Interpretation of WAO Results

Wet air oxidation of phenol solutions can be assumed to take place in the bulk liquid. This assumption is based on previous studies by Zimmermann and other workers of WAO, where no reaction was observed in the absence of liquid phase.

The reaction thus proceeds as oxygen diffuses through the gas, the gas-liquid interface, and the liquid to reach the reaction site. The overall rate of reaction thus could be limited by either or both of the mass transfer resistances and/or the rate of the chemical reaction.

The gas phase resistance has been studied by Yoshida^{27,28} under similar conditions and they found that this resistance was negligible. Thus the complexity of the determination of rate-controlling step can be reduced to the study of the relative influences of liquid side mass transfer of oxygen, and chemical reaction on the overall rate of reaction.

If the overall rate of reaction is controlled only by the rate of mass transfer of oxygen in the liquid phase, or if the chemical reaction is very fast, then the rate expression can be written²⁹ as:

$$r = k_1 \cdot a \cdot V_R (C^* - C_{O_2}) \quad (1)$$

where k_1 is the liquid phase mass transfer coefficient of oxygen, a is the bubble surface area per unit volume of reactor, V_R is the reactor volume, and C^* and C_{O_2} are the saturation and the actual oxygen concentrations. Here r is expressed as moles of oxygen transferred per hour. To express the rate with respect to moles of phenol converted per hour:

$$r = k_1 \cdot a \cdot b \cdot V_R (C^* - C_{O_2})$$

with b being the stoichiometric ratio of moles phenol to moles O_2 . As a very fast chemical reaction is assumed, then all the oxygen reaching the reaction site will be consumed immediately and therefore $C_{O_2} \approx 0$. The rate expression then becomes:

$$r = k_1 \cdot a \cdot b \cdot V_R \cdot C^*$$

Keeping the air flow rate constant at reactor conditions (constant superficial gas velocity) and also operating at the same stirring speed, for a fixed temperature, the mass transfer term $k_1 \cdot a$ can be assumed to remain the same. Thus the rate of reaction would be a linear function of C^* . From Henry's Law for gas liquid systems at equilibrium:

$$P_{O_2} = H \cdot C^*$$

and for the rate expression it can be written:

$$r = k_1 \cdot a \cdot b \cdot V_R \cdot \frac{P_{O_2}}{H} \quad (2)$$

This shows that if the mass transfer of oxygen is the only factor controlling the overall rate of reaction, then the rate would be directly proportional to the partial pressure of oxygen.

In the case where the overall rate of reaction is controlled by chemical reaction, it will be of the form:

$$r = k_r \cdot V_R \cdot C_{O_2}^m \cdot C_{Ph}^n \quad (3)$$

where k_r is the reaction rate constant, C_{Ph} is the reactor concentration of phenol, and m and n are exponents. In this case where it is assumed that the rate of mass transfer of oxygen is much faster than the chemical reaction, then the oxygen concentration in the liquid phase can be assumed to be the saturation concentration or:

$$C_{O_2} = C^* = \frac{P_{O_2}}{H}$$

and

$$r = k_r \cdot V_R \cdot \frac{P_{O_2}}{H} \cdot C_{Ph}^n \quad (4)$$

Again the rate of reaction is to some extent proportional to partial pressure of oxygen.

But maintaining the pressure and increasing the temperature would affect the rate of reaction largely if the reaction rate expression is of the form of Equation (4), and would have small effects on reaction rate if it follows Equation (2). This comes from the fact

that of two rate constants $\frac{k_1}{H}$ and $\frac{k_r}{H^m}$, it is the latter that is more sensitive to temperature changes.

2. Discussion of Results

The results of runs without the presence of air showed that there was not any phenol-disappearance due to the thermal treatment of the solutions.

The reaction did not proceed at room temperature or at 120 °C, while a sudden increase in the rate of reaction was noticed at a temperature of 200 °C. This suggested that in the WAO process there was a lower level of temperature below which the reaction would not proceed.

It can be seen from Figures 8, 9, 10 and 11 that the conversion behaves differently at higher pressures than in the lower range. At higher pressures (over 1,500 psig.), the conversion tends to remain unchanged for further increases in pressure. This indicates that the overall rate of reaction also remains constant under these conditions and thus the overall rate is not controlled by the rate of mass transfer of oxygen, rather it is controlled by the rate of chemical reaction which is limited by the low phenol concentration in the reactor.

Considering the lower pressure range, the conversion is lower and becomes more pressure sensitive as the reactor pressure decreases, and drops drastically at pressures very close to the vapor pressure of

water at that temperature. While these observations are in good agreement with the previously developed Equation (4) they further support the assumption that reaction takes place in the liquid phase which was also reported by Zimmermann. However in this region of lower pressures (less than 1,500 psig.) should the reaction be controlled solely by mass transfer, the overall rate of reaction would be linearly dependent on partial pressure of oxygen and the ratio of rates at two different pressures would be equal to the ratio of partial pressures of oxygen. Table 1 shows the rates of reaction for two different pressures at three different residence times. It can be seen from this table that the rate of reaction increases approximately half as much as partial pressure of oxygen at these conditions. The results for the runs at 250°C are similar. This shows that although the role of mass transfer in controlling the overall rate of reaction becomes more significant with decreasing pressure, the rate of reaction is not controlled solely by mass transfer and thus the control mechanism is complex.

The effect of temperature can be studied by considering Figures 13 and 14 where an increase of 50°C in temperature increased the conversion at higher pressures and decreased it at lower pressures.

In the lower pressure zone (around 800 psig.) a decrease of 11.9% for conversion is observed when the temperature increased from 200 to 250°C. The fact that at any pressure an increase in temperature calls for a decrease in partial pressure of oxygen (as the vapor

Table 1

Reaction Rates (moles/l.hr) at Different Pressures

Data is taken from Tables 5 and 6 of the Appendix

| Liquid feed rate (ml/hr.) | Reaction Rate moles/l.hr | | $\frac{\text{Rate}_{1500}}{\text{Rate}_{800}}$ |
|------------------------------|-----------------------------|----------------|--|
| | P = 800 psig. | P = 1500 psig. | |
| 2000 | 0.00804 | 0.00819 | 1.019 |
| 4000 | 0.01572 | 0.01614 | 1.027 |
| 6000 | 0.01810 | 0.01989 | 1.098 |
| | | | <u>1.048 average value</u> |

at 200 °C, 800 psig; $P_{O_2} = 124$ psiaat 200 °C, 1500 psig; $P_{O_2} = 271$ psiaand
$$\frac{(P_{O_2})_{1500}}{(P_{O_2})_{800}} = 2.18$$

therefore:

$$\left(\frac{\text{Rate}_{1500}}{\text{Rate}_{800}} \right) / \left(\frac{P_{O_2, 1500}}{P_{O_2, 800}} \right) \approx 0.5$$

Similar calculations for runs at 250 °C showed:

$$\left(\frac{\text{Rate}_{1500}}{\text{Rate}_{800}} \right) / \left(\frac{P_{O_2, 1500}}{P_{O_2, 800}} \right) = 0.4$$

pressure of water would be increased) and also any change of P_{O_2} would affect both; the rate of chemical reaction and mass transfer, therefore temperature has also one inverse effect on the rates and only it is the combined effect that can be seen from these figures. This inverse effect would be less at higher pressures. But at lower pressures where P_{O_2} and subsequently conversion becomes very sensitive to pressure changes, the inverse effect of decreasing the conversion becomes significant and thus such 11.9% decrease can be explained.

The above could be further explained when the conversion is studied with respect to partial pressure of oxygen as is done in Figure 15. This figure shows that the conversion is increased by approximately 16% for all pressures and slightly to an increasing degree at higher pressures when the temperature rises from 200 to 250 °C. Under similar conditions Ferguson's¹³ study in an unmixed reactor showed an average increase of 15.1% for conversion.

As for reactions having activation energies of 11^{30} Kcal/gm mole, an increase of 50 °C in temperature would increase the reaction rate by a factor of 3.07 when the temperature rises from 200 to 250 °C (see the Appendix). But the results of this study shows approximately half as much increase for the rates at these conditions and thus indicating that the overall rate of reaction is partly chemically controlled for all pressures and to an increasing degree at higher pressures.

It can be concluded that reaction control mechanism under the

conditions studied in this work remains complex for all pressures and thus a control mechanism involving both of the resistances in series should be considered.

Assuming this, a general form of expression for conversion was developed (see the Appendix) as:

$$\text{Conversion} = \frac{\Delta C_{\text{Ph}}}{C_{\text{Ph}(0)}} = \frac{\tau}{0.5C_{\text{Ph}(0)}} k_r \cdot \left(\frac{0.21(P-p_w)}{H} - \frac{0.8 \Delta C_{\text{Ph}}}{k_1 \cdot a \cdot b \cdot \tau} \right)^{m_{\text{Ph}}} C_{\text{Ph}}^n \quad (5)$$

The effects of different variables on conversion can be seen from this equation.

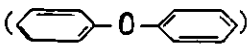
The parameters in the above equation can be calculated using a computer program which fits non-linear models to experimental data. Such a program using a successive linear least squares method was employed and the initial estimates were based on calculations assuming a first order kinetics. The results of the run on the computer is given in the Appendix. These results show that the rate of reaction can be represented by Equation (5) with $m = 0.85$ with respect to oxygen and $n = 1.54$ with respect to phenol. The model also provided the value of the rate constant of oxidation and the mass transfer product of $k_1 \cdot a$ for runs at 200 °C.

The values thus found for m and n for the complete oxidation of phenol in aqueous solutions suggest the formation of some intermediary or partially oxidized products. These products tend to appear, as is observed by Schmidt,¹² at high phenol feed concentrations

and lower temperatures and their rate of decomposition increases by increasing temperature. At practical operating conditions of WAO (high conversions) their presence in the end products becomes much limited and can hardly be detected.

The thorough investigation of the above aspect, linked to other complications of WAO of phenol such as the determination of the location of reaction zone, is quite complex and requires a long-term investigation which is beyond the scope of this work.

A comparison of the experimental results obtained in this study in a mechanically agitated reactor with the one in an unmixed reactor by Ferguson¹³ shows that the rates of reaction and the conversion of phenol remains almost the same at these two conditions. The use of mechanical agitation will improve the conversion only for pressures very close to the vapor pressure of water at the reactor temperature. But this is also the region of erratic operation of WAO, as in the WAO process the presence of liquid water is an essential factor for the process to proceed. Therefore the use of a mechanically agitated reactors are not advantageous.

For some runs at 200 °C with feed concentrations of 4,000 mg/l the reactor effluent turned brownish. The color tint disappeared by increasing pressures. Further studies of the effluent stream for these runs on Chromotograph showed the presence of diphenyl ether () at these conditions. The maximum concentration of P.E. was found to be 400 mg/l. This was done by comparing with a purchased Standard Solution of Phenol Ether. Chromatograms also

showed traces of other materials, possible other phenolic condensates which were too little for analytical purposes. These are the same products as Schmidt and other workers in WAO of phenol have been observed.

Acetic acid was also identified in the effluent at about the same conditions where phenolic tars were formed. The maximum acetic acid concentration was observed for run #19 and measured on the chromatograph to be 150 mg/l, much lower than 6,000 mg/l found by Schmidt. The large difference can be explained by the fact that very high phenol feed concentrations (up to 50,000 mg/l) were used in his study. The production of acetic acid decreased by increasing temperature and pressure.

Analysis on the nature of the gases leaving the reactor showed that it is nearly saturated with water at reactor conditions. The above obtained results in this study indicates the applicability of WAO process and the operating conditions at which the process could be best achieved for removing phenol in aqueous solutions. These results compare favorably in terms of phenol conversions to the previous works of Schmidt and Ferguson. The operation of WAO at temperatures higher than the maximum temperature used in this study (250 °C) would likely provide higher conversions and temperatures of 120 °C and lower is proved to be beyond the operating range of WAO process. The formation of by-products appeared mostly at lower temperatures and pressures where the degree of phenol oxidation was also lower. Thus the WAO process not only maintains high conversions but also

produces products of high degree of purity at higher pressure and temperatures.

A comparison of the results of different WAO studies on many different types of waste streams shows the adequacy of WAO process in treating different materials with equal ease. It is also shown previously that there exist a trade-off between pressure and liquid residence time at high conversions. Thus for conditions where concentration of organic material to be treated and the feed volume are not stable, WAO process has clear advantages.

At the conditions of this study the process was a user of energy although it was faced by an exothermic reaction. This was due to very low feed concentrations and rather high operating pressure and temperature. The use of higher feed concentration (about 5 times the ones in this work) in Zimmermann's study with different type of feed, proved that the overall operation could be energetically self-sufficient or even a producer of net amount of energy in some cases.

CONCLUSIONS

1. The process of wet air oxidation was applied to the continuous oxidation of phenol in dilute aqueous solutions in a mechanically agitated reactor. The process proved to be effective in converting of up to 96.83% of the treated phenol mostly to carbon dioxide and water.
2. The obtained results of this study favorably corresponds to the previously obtained results of Schmidt¹² in a batch system and to a good extent duplicated those obtained in a continuous non-mechanically agitated reactor.¹³
3. The results obtained in this work show that the reaction control mechanism remains complex over the range of the practical application of the WAO process. The role of chemical reaction in the overall reaction rate increased by increased pressures while the role of mass transfer of oxygen to the reaction site increased by decreased pressures. A comparison of the results obtained in this work under mechanical agitation with the previous one without it indicates that under these conditions the use of mechanical agitation can not be justified.
4. The gas-liquid holdup ratio for this type of reactors was shown to be not negligible. This factor was found experimentally in this work and was about 20% for most conditions.

REFERENCES

1. Henshaw, T.B., "Adsorption/Filtration Plant Cuts Phenols from Effluents", Chemical Engineering, May 31, 1971, p. 48.
2. Ellsworth Hackman, E., "Toxic Organic Chemicals", Noyers Data Corporation, N.J., 1978, pp. 36-63.
3. Beltrame, P., "Kinetics and Byproducts of the Liquid Phase Oxidation of Phenol to p-Benzoquinone Catalysed by CuCl_2 ", Ind. Eng. Chem. Prod. Res. Dev., 18, No. 3, 1979, pp. 208-211.
4. Pradt, L. A., "Developments in Wet Air Oxidation", Chemical Engineering Progress, 68, No. 12, 1972 pp. 72-77.
5. Kirk Brown, C., "Wetoxidation-Heat Without Flame" Water and Pollution Control, December 1974, pp. 36-37.
6. Beychok, M.R., "Aqueous Waste from Petroleum and Petro-chemical Plants", John Wiley & Sons Inc., 1974, p. 14.
7. Irving Sax, N., "Dangerous Properties of Industrial Materials", Reinhold Book Corp., N.Y., 1968, p. 1007.
8. Zimmermann, F. J., "Sewage Sludge Treatment by Wet Air Oxidation", Proceedings of Thirteenth Industrial Waste Conference, May 5, 6, 7, 1958, Series No. 96, Engineering Bulletin.
9. Zimmermann, F.J., United States Patent 2,824,058. 1944.
10. Schatzberg, P., Jackson, D.F., "Experimental Investigation of the Wet Oxidation Destruction of Shipboard Waste Streams, Inter-society Conference on Environmental Systems, Seattle, 1974, ASME publication 74-ENAs-5, 11 pages.
11. Zimmermann, F.J., "Wet Air Combustion", Industrial Water & Wastes, August 1961, pp. 102-106.
12. Schmidt, L.I., "Liquid Phase Oxidation of Phenol in Waste Waters at Elevated Temperatures and Pressures", Zhurnal Prikladnoi Khimi, 43, No. 9, 1970, pp 2123-2125.

13. Ferguson, D.R., "Continuous Oxidation of Phenol in Water at Elevated Temperatures and Pressures", M.A.Sc. Thesis, Department of Chemical Engineering. U. of Ottawa, December 1972.
14. Schulze-Forster, A., Hasse, L.W., "A Contribution to the Removal of Phenol in Waste Water", *Gesundh-Ing.*, 56, 1933, pp 608-610.
15. Stepanyan, I.S., Vinokour, S., Padaryan, I.A., "The Liquid Phase Oxidation of Phenol, Methanol, and Formaldehyde Suitable for the Purification of Waste Waters", *Khimicheskaja Promyshlennost (Moscow)*, 48, 1972, pp 430-432.
16. Kramarenko, S.S., "The Mechanisms and the Kinetics of the Combustion Process of Substances Suspended or Dissolved in Water under Conditions of Incomplete Evaporation", *Chemical Abstract No. 33795g.*, 71, 1969, p. 289.
17. Walsh, M.A., Katzer, J.R., "Catalytic Oxidation of Phenol in Dilute Concentrations in Air", *Ind. Eng. Chem. Process Des. Dev.*, 12, No. 4, 1973. pp. 477-481.
18. Sadana, A. Katzer, J.R., "Catalytic Oxidation of Phenol in Aqueous Solutions over Copper Oxide", *Ind. Eng. Chem. Fundam.*, 13, No. 2, 1974, pp. 127-134.
19. Sideman, S., Hortascu, O., Fulton, J.W., "Mass Transfer in Gas-Liquid Contacting Systems", *Ind. Eng. Chem.*, 58, No. 7, 1966, pp. 32-47.
20. Westerterp, K.R., Van Dierendock, L.L., de Kraa, A.J., "Interfacial Areas in Agitated Gas-Liquid Contactors", *Chem. Eng. Sc.*, 18, 1963, pp. 157-175.
21. Linek, V., Mayrhoferova, J., "The Chemical Method for the Determination of Interfacial Area", *Chem. Eng. Sc.*, 24, 1969, pp. 481-496.
22. Sridhar, I., Potter, O.E., "Gas Holdup and Bubble Diameters in Pressurized Gas-Liquid Stirred Vessels", *Ind. Ing. Chem. Fundam.*, 19, 1980, pp. 21-26.
23. Himmelblau, D.M., "Solubilities of Inert Gases in Water", *J. Chem. Eng. Data*, 5, No. 1, 1960, pp. 10-15.

24. St.Dennis, C.E., Fell, C.J.D., "Diffusivity of Oxygen in Water", Canadian J. Chem. Eng., 49, No. 6, 1971, p. 885
25. Annual Book of ASTM Standards, part 23, American Society for Testing and Materials, Philadelphia, 1970, pp 519-820.
26. Zimmermann, F.J., "The Zimmermann Process and its Applications in the Pulp and Paper Industry", Tappi, 43, No. 8, 1960, pp. 710-715.
27. Yoshida, F., Ikeda, A., "Oxygen Absorption Rates in Stirred Gas-Liquid Contactors", Ind, Eng. Chem., 52, No. 5, 1960, pp 435-438.
28. Yoshida, F., Kiyomi, A., "Performance of Gas Bubble Columns", A.I. Ch. E. Journal, 11, No.1, 1965, pp. 9-13
29. Levenspied, O., "Chemical Reaction Engineering", John Wiley & Sons Inc., N.Y., 1972, p. 413.
30. Pruden, B.B., Ferguson, D.R., "Removal of Phenol in Waste Water by Wet Air Oxidation", Proc. 8th Canadian Symp. on Water Pollution Res., University of Waterloo, 8, 1973, p. 148.

APPENDICES

APPENDIX 1. Experimental Data

Table 2 shows the details of experimental runs in Gas Holdup Analysis.

Tables 3, 4, 5 and 6 show the experimental data for the calculation of phenol conversion.

Table 7 is giving the partial pressure of oxygen at two different temperatures for different reactor total pressures.

Table 2

| Run No. | T (°C) | P (psig) | L. Flow (cm ³ /hr) | A. Flow (ft ³ /hr) | R.P.M. | L. (cm ³) | V _L (cm ³) | H/U % | Comments |
|---------|--------|----------|-------------------------------|-------------------------------|--------|-----------------------|-----------------------------------|-------|----------------------|
| 1 | 25 | 0.0 | 4,000 | 0.6 | 1880 | 2780 | 2779.98 | 23.79 | air flow was erratic |
| 2 | 25 | 800. | 4,000 | 0.6 | 1880 | 2900 | 2899.98 | 20.50 | |
| 3 | 25 | 1,500. | 4,000 | 0.6 | 1890 | 2870 | 2869.98 | 21.33 | |
| 4 | 25 | 0. | 6,000 | 0.6 | 1890 | 2970 | 2969.98 | 18.59 | |
| 5 | 25 | 2,200. | 4,000 | 0.6 | 1870 | 2850 | 2849.98 | 21.88 | |
| 6 | 25 | 800. | 6,000 | 0.6 | 1880 | 2990 | 2989.98 | 18.04 | |
| 7 | 70 | 800. | 6,000 | 0.6 | 1890 | 2890 | 2947.64 | 19.20 | |
| 8 | 120 | 800. | 6,000 | 0.6 | 1880 | 2760 | 2924.49 | 19.83 | |
| 9 | 158 | 800. | 6,000 | 0.6 | 1850 | 2725 | 2994.43 | 17.92 | |
| 10 | 200 | 800. | 6,000 | 0.6 | 1820 | 2550 | 2948.85 | 19.17 | |
| 11 | 120 | 800. | 4,000 | 0.6 | 1880 | 2740 | 2903.26 | 20.42 | |
| 12 | 120 | 800. | 8,000 | 0.6 | 1860 | 2800 | 2966.96 | 18.67 | |
| 13 | 120 | 800. | 2,000 | 0.6 | 1890 | 2600 | 2754.63 | 24.49 | |
| 14 | 120 | 800. | 6,000 | 0.35 | 1880 | 2785 | 2951.03 | 19.11 | |
| 15 | 120 | 800. | 6,000 | 0.10 | 1890 | 2860 | 3030.66 | 16.92 | |
| 16 | 120 | 800. | 6,000 | 0.75 | 1890 | 2750 | 2913.88 | 20.12 | |
| 17 | 120 | 800. | 6,000 | 0.6 | 0. | 3080 | 3264.21 | 10.52 | |
| 18 | 120 | 800. | 6,000 | 0.6 | 525. | 3095 | 3280.14 | 10.08 | |
| 19 | 120 | 800. | 6,000 | 0.6 | 800. | 3030 | 3211.13 | 11.98 | |
| 20 | 120 | 2,200. | 8,000 | 0.6 | 1830. | 2460 | 2606.01 | 28.56 | Phenol Solution |
| 21 | 120 | 800. | 6,000 | 0.6 | 1130. | 2970 | 3147.43 | 13.72 | |
| 22 | 120 | 800. | 6,000 | 0.6 | 1400. | 2830 | 2998.81 | 17.80 | |
| 23 | 200 | 2,200. | 4,000 | 0.6 | 1880. | 2410 | 2784.30 | 23.68 | |

Table 3

Summary of Runs 1 to 12

| Run No. | Liquid Flow (ml/hr) | Feed Concentration (mg/l) | Temperature (°C) | Pressure (psig) | Agitation Speed (r.p.m.) | Reaction Rate (g mole/1.hr) | Phenol Conversion (%) | Comments on Run |
|---------|---------------------|---------------------------|------------------|-----------------|--------------------------|-----------------------------|-----------------------|-----------------|
| 1 | 8600 | 1142.2 | 28.5 | 0.0 | 0.0 | 0 | 0 | No air |
| 2 | 8250 | 1052.1 | 28 | 2200 | 10.0 | 0 | 0 | No air |
| 3 | 8300 | 1001.1 | 132 | 2200 | 0.0 | 0 | 0 | No air |
| 4 | 8300 | 1059.1 | 143 | 2200 | 1830 | 0 | 0 | No air |
| 5 | 4000 | 1038.8 | 25 | 0.0 | 1880 | 0 | 0 | |
| 6 | 4000 | 1038.8 | 25 | 800 | 1850 | 0 | 0 | |
| 7 | 4000 | 1038.8 | 25 | 1500 | 1850 | 0 | 0 | |
| 8 | 4000 | 1038.8 | 25 | 2200 | 1850 | 0 | 0 | |
| 9 | 6000 | 1055.48 | 25 | 0.0 | 1750 | 0 | 0 | |
| 10 | 6000 | 1055.48 | 25 | 800 | 1750 | 0 | 0 | |
| 11 | 6000 | 1055.48 | 25 | 1500 | 1750 | 0 | 0 | |
| 12 | 6000 | 1055.48 | 25 | 2200 | 1750 | 0 | 0 | |

Table. 4

Summary of Runs 13 to 18

| Run No. | Liquid Flow (ml/hr) | Feed Concentration (mg/l) | Temperature (°C) | Pressure (psig) | Agitation Speed (r.p.m.) | Effluent Concentration (mg/l) | Phenol Conversion (%) | Comments on Run |
|---------|---------------------|---------------------------|------------------|-----------------|--------------------------|-------------------------------|-----------------------|--------------------------|
| 13 | 8000 | 960.68 | 120 | 800 | 1820 | 960.68 | 0 | |
| 14 | 8000 | 960.68 | 120 | 1500 | 1820 | 960.68 | 0 | |
| 15 | 8000 | 960.68 | 120 | 2200 | 1820 | 960.68 | 0 | |
| 16 | 8000 | 3992.1 | 120 | 800 | 1820 | 3992.1 | 0 | |
| 17 | 8000 | 3748.9 | 120 | 1500 | 1820 | 3748.9 | 0 | |
| 18 | 8000 | 3748.9 | 120 | 2200 | 1830 | 3748.9 | 0 | also used for gas holdup |

6

7

Table 5.

Summary of Phenol runs 19 to 31

| Run No. | Liquid Flow (ml/hr) | Feed Concentration (mg/l) | Temperature (°C) | Pressure (psig) | Agitation Speed (r.p.m.) | Reactor Concentration (mg/l) | Conversion (%) | Comments |
|---------|---------------------|---------------------------|------------------|-----------------|--------------------------|------------------------------|----------------|---------------------|
| 19 | 6000 | 3884.0 | 200 | 800 | 1820 | 1028.21 | 73.5 | dark brown effluent |
| 20 | 6000 | 3884.0 | 200 | 1500 | 1820 | 312.58 | 91.95 | brownish effluent |
| 21 | 6000 | 3884.0 | 200 | 2200 | 1800 | 141.23 | 96.30 | |
| 22 | 8000 | 3884.0 | 200 | 2200 | 1800 | 309.79 | 92.02 | |
| 23 | 2000 | 1465.36 | 200 | 800 | 1800 | 87.66 | 94.02 | |
| 24 | 2000 | 1465.36 | 200 | 1500 | 1800 | 61.18 | 95.82 | |
| 25 | 2000 | 1465.36 | 200 | 2200 | 1800 | 46.48 | 96.83 | |
| 26 | 4000 | 1465.36 | 200 | 800 | 1800 | 117.67 | 91.97 | |
| 27 | 4000 | 1465.36 | 200 | 1500 | 1810 | 81.94 | 94.41 | |
| 28 | 4000 | 1465.36 | 200 | 2200 | 1810 | 75.36 | 94.86 | |
| 29 | 6000 | 1222.02 | 200 | 800 | 1800 | 187.46 | 84.66 | |
| 30 | 6000 | 1222.02 | 200 | 1500 | 1800 | 85.30 | 93.02 | |
| 31 | 6000 | 1222.02 | 200 | 2200 | 1800 | 76.86 | 93.71 | |

Table 6

Summary of Phenol runs 32 to 35

| Run No. | Liquid Flow (ml/hr) | Feed Concentration (mg/l) | Temperature (°C) | Pressure (psig) | Agitation Speed (r.p.m.) | Reactor Concentration (mg/l) | Conversion (%) | Comments |
|---------|---------------------|---------------------------|------------------|-----------------|--------------------------|------------------------------|----------------|--------------------------|
| 32 | 8200 | 4449.41 | 250 | 800 | 1800 | 1748.23 | 60.71 | brown effluent and foamy |
| 33 | 8000 | 4449.41 | 250 | 1500 | 1800 | 315.64 | 92.91 | |
| 34 | 8000 | 4449.41 | 250 | 1500 | 1800 | 312.35 | 92.98 | |
| 35 | 8000 | 4449.41 | 250 | 2200 | 1800 | 261.63 | 94.22 | |

Table 7

Partial Pressures of Oxygen

| | | |
|-------------------------------|-----|-----|
| Temperature, °C | 200 | 250 |
| Vapor Pressure of Water, psia | 225 | 516 |

Assuming the vapor phase in reactor is water saturated, the following table can be constructed while:

$$P_{O_2} = 0.21(P - P_w)$$

| Total Pressure (psia) | Temperature (°C) | |
|--------------------------|---------------------|-----|
| | 200 | 250 |
| 815 | 124 | 50 |
| 1515 | 271 | 197 |
| 2215 | 418 | 344 |

APPENDIX 2. Gas Phase Saturation

The purpose of experiments in this part was to investigate vapor phase composition in the reactor. This was needed in making corrections on gas holdup or the phenol concentration for actual reactor conditions as all the samples were taken at atmospheric pressure and room temperature.

The experiments were carried out at 800 psig and temperatures of 200 and 250 °C. Reactor was a 1.0 liter "High Pressure" stainless steel reactor without mechanical agitation supplied by Pressure Product Industries. The reactor was operated using all process equipment used in the phenol runs. The feed was distilled water.

The flow rate of liquid water from reactor outlet was measured from the time when the system was at steady-state operation and the liquid feed water shut-down. Also the reactor temperature, pressure, and the air flow rate were maintained the same. The amount of water collected at these conditions could be represented the amount of water in the vapor phase of the reactor.

The results of these experiments are tabulated in Tables 9 and 10. Figures 16 and 17 are based on these tabulations. Figure 16 shows the rate of water in gas phase of the reactor exit stream with respect to time at 200 °C. The same curve at 250 °C is shown by Figure 17.

The rate of water removal in a saturated vapor phase at reactor conditions is calculated as follows:

Air flow: $0.5 \text{ ft}^3/\text{hr}$ at condition

Volume at S.T.P.: $0.5 \cdot \frac{P \cdot 273}{14.7 \cdot T(^{\circ}\text{K})} \text{ ft}^3$

One gm mole at S.T.P. 22.4 liters or
 $\frac{22.4}{28.3} \text{ ft}^3$

Moles of air: $0.5 \cdot \frac{P}{T} \cdot \frac{273}{14.7} \cdot \frac{28.3}{22.4} \text{ gm mole/hr.}$
 $= 11.73 \cdot \frac{P}{T} \text{ gm mole/hr.}$

By the use of Raoult's Law, it can also be written:

$$\frac{\text{Moles of Water}}{\text{Moles of Air}} = \frac{\bar{P}_w}{P_{\text{air}}} = \frac{\bar{P}_w}{P - \bar{P}_w}$$

and

$$\begin{aligned} \text{gm water/hr} &= 18 : \text{moles water} \\ &= 18 \text{ moles air} \cdot \frac{\bar{P}_w}{P - \bar{P}_w} \end{aligned}$$

thus

$$\text{gm water/hr} = 211 \cdot \frac{P}{T} \left(\frac{\bar{P}_w}{P - \bar{P}_w} \right) \quad (6)$$

This equation gives the grams of water in the vapor that is in equilibrium with the air flow rate of $0.5 \text{ ft}^3/\text{hr}$ at reactor conditions. In table 8

this amount is calculated for some specified conditions using Equation (6).

Table 8

| T (°C) | P (psia) | gm water/hr |
|--------|----------|-------------|
| 200 | 815 | 138 |
| 200 | 1515 | 118 |
| 200 | 2215 | 112 |
| 250 | 815 | 793 |
| 250 | 1515 | 374 |
| 250 | 2215 | 314 |

From Figure 16 the rate of water collected drops very quickly from 2000 to about 120 ml/hr. after the feed stopped. This gives the amount of water carried in the gas phase of the reactor at 200 °C and 800 psig. If the gas was saturated at these conditions, the rate should be 138 ml/hr. (extracted from Table 9), slightly different from the actual figure of 120 ml/hr. In this case the degree of saturation would be 87%.

The composition of gas phase in the reactor at 250 °C. and 800 psig can be obtained from Figure 17 where again the outlet water flow rate was measured after stopping the liquid feed rate of 2,000 ml/hr. The amount was found to be 350 ml/hr. and far from the saturation condition of 792 ml/hr. The degree of saturation here was 44.2%.

We know that reaching, even closely, to equilibrium condition would need a great deal of time, but how much is the contact time of the air and liquid water in this experiment?

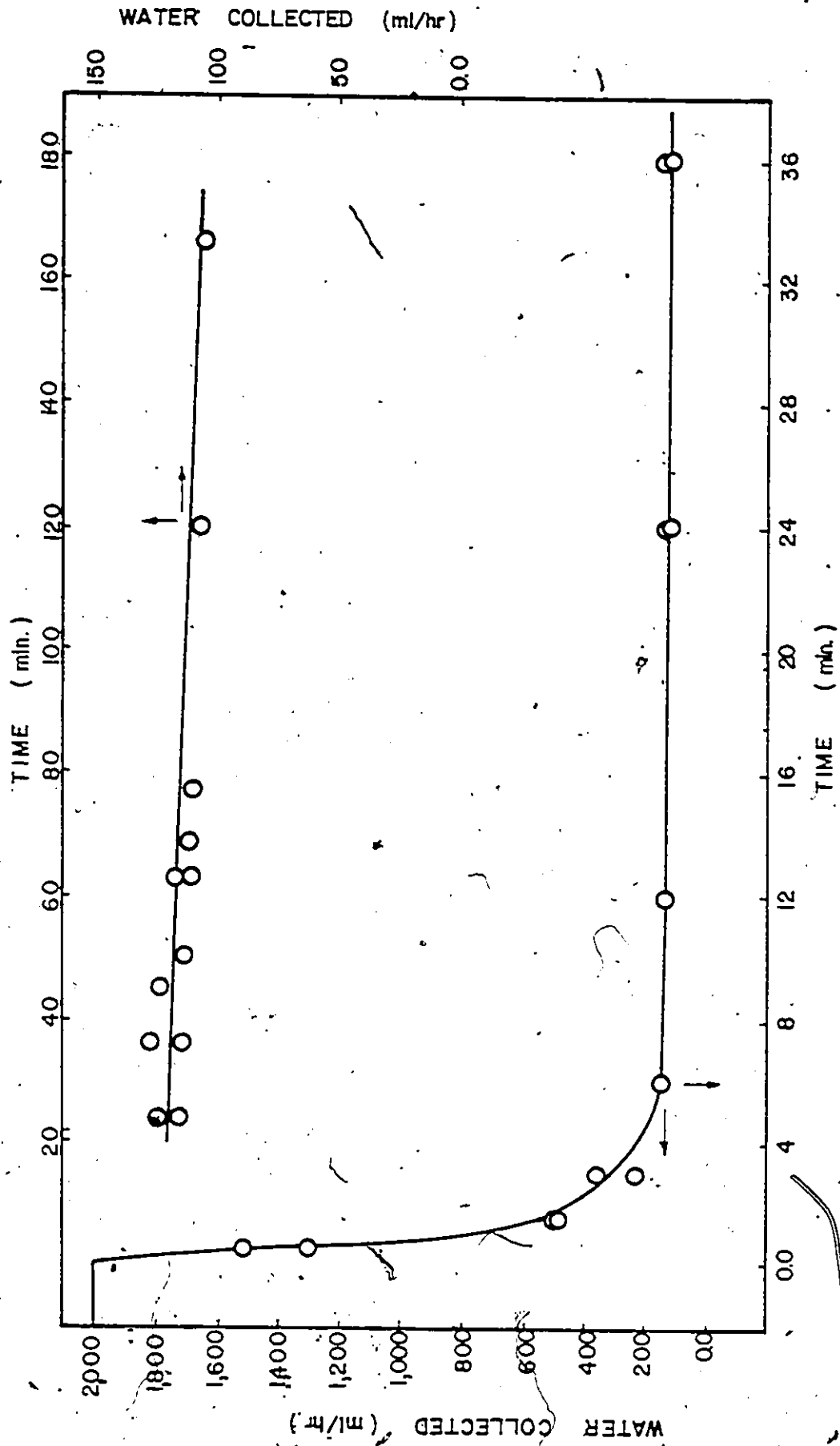


Figure 16 Rate of Water vs. Time at 200 °C and Reactor Pressure of 800 psig

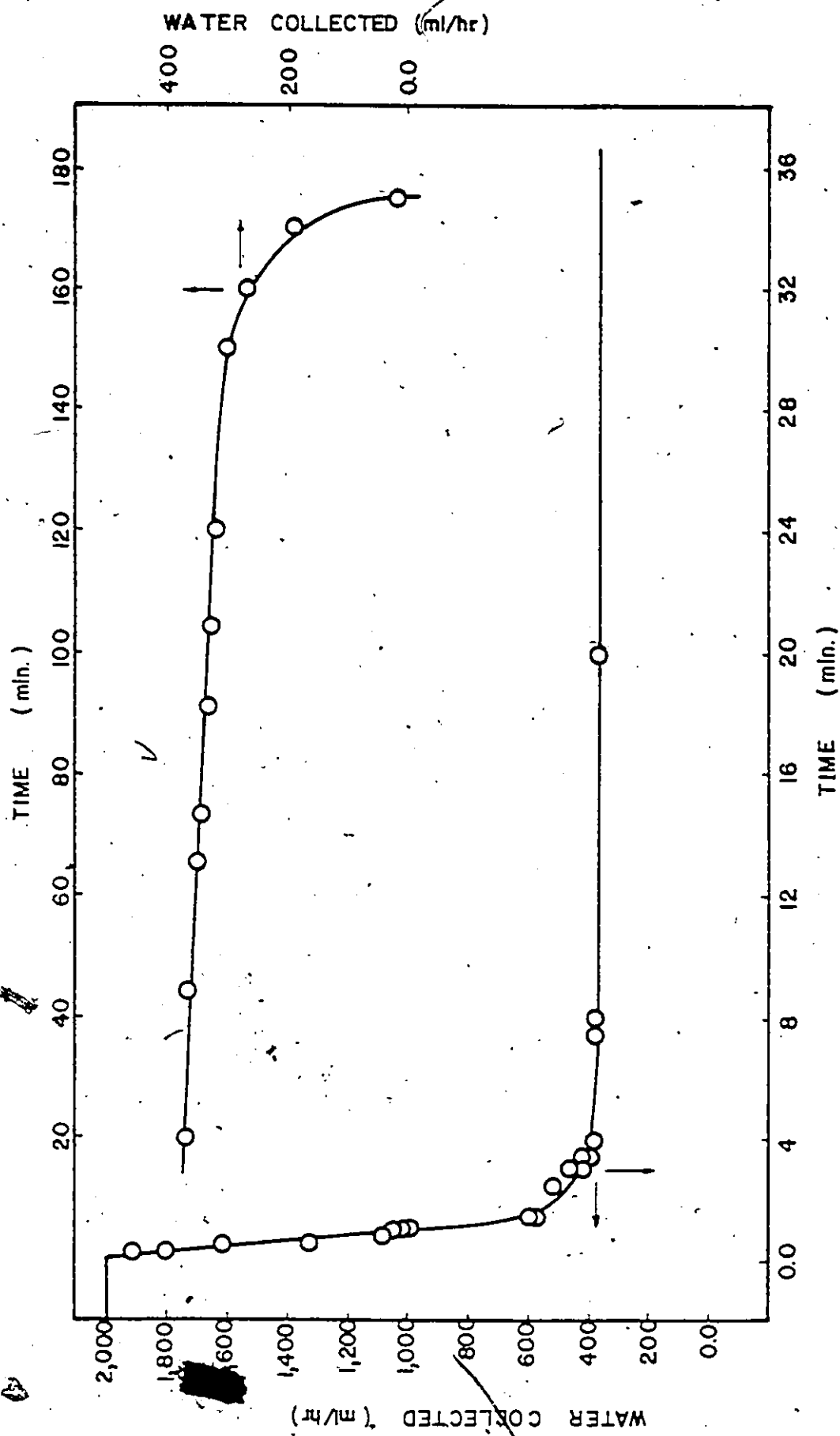


Figure 17 Rate of Water vs. Time at 250 °C and Reactor Pressure of 800 psig

Reactor volume = 1000 ml

Assumed air H/U = 10 %

Air volume = 100 ml

Air flow rate = $\frac{0.5 \times 28300}{60}$ ml/min.

Air contact time = $\frac{\text{Air Volume}}{\text{Air Flow}}$

$$= \frac{100 \times 60}{0.5 \times 28300} = 0.42 \text{ min.}$$

which is a very short contact time. Even assuming 92% by volume air in the reactor, would bring the contact time to 4.0 minutes. This can be a reason for the vapor phase in the reactor, at pressures close to the vapor pressure of water at that temperature, to be not saturated. Meanwhile the vapor phase can be assumed saturated at conditions of higher pressures or lower temperatures.

Table 9

| Time (Min.) | Rate of Water (ml/hr) | Time (Min.) | Rate of Water (ml/hr) |
|-------------|-----------------------|-------------|-----------------------|
| 0.5 | 1290 | 36 | 127 |
| | 1500 | | 113 |
| 1.5 | 486 | 45 | 123 |
| | 480 | 50 | 113 |
| 3 | 360 | 63 | 117 |
| | 255 | | 110 |
| 6 | 135 | 69 | 110 |
| | 132 | | 111 |
| 12 | 120 | 77 | 108 |
| | 127 | 120 | 107 |
| | | 166 | 105 |
| 24 | 123 | | |
| | 116 | | |

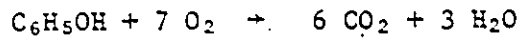
Table 10.

| Time (Min.) | Rate of Water (ml/hr) | Time (Min.) | Rate of Water (ml/hr) |
|----------------|--------------------------|----------------|--------------------------|
| 0.25 | 1920 | 3.5 | 420 |
| | 1800 | | 410 |
| 0.5 | 1320 | 4 | 380 |
| | 1620 | 7.5 | 380 |
| | | 8 | 379 |
| 0.75 | 1080 | | |
| 1.0 | | 20 | 368 |
| | 1020 | 44 | 365 |
| | 1000 | 65 | 348 |
| | 1050 | 73 | 342 |
| 1.5 | | 91 | 336 |
| | 600 | 104 | 328 |
| | 570 | 120 | 318 |
| 2.5 | | 150 | 300 |
| | 520 | 160 | 270 |
| 3.0 | 465 | 170 | 190 |
| 8.0 | 420 | 175 | 20 |

APPENDIX 3. Calculation Methods

I. Stoichiometry

The complete oxidation of phenol is given by the following equation:



The molecular weight of phenol is 94 and of oxygen 32. The theoretical oxygen demand of a phenol solution of concentration C mg/l is:

$$7 \cdot C \cdot \frac{32}{94} = 2.4 \text{ C mg/l.}$$

II. Calculation of Required Air

The calculation for required air is made on a typical run with the following conditions:

| | |
|--------------------|-------------|
| temperature | 200 °C |
| pressure | 2,200 psig |
| feed concentration | 4,000 mg/l |
| feed rate | 6,000 ml/hr |

from the stoichiometry, the theoretical oxygen demand of such a solution is:

$$\begin{aligned} 2.4 \times 4000 &= 9600 \text{ mg/l.} \\ &= 9.6 \text{ gm/l.} \end{aligned}$$

Based on one hour, 6000 ml. of the solution will be oxidized, then the rate of required oxygen is:

$$9.6 \times 6 = 57.6 \text{ gm/hr. oxygen}$$

Since air is approximately 23.3% by weight oxygen, then air required rate is:

$$\frac{57.6}{0.233} = 247.2 \text{ gm/hr. air}$$

The density of air at 25 °C and atmospheric pressure is 0.00141 gm/cm³.

Thus the rate of required air flow is:

$$\begin{aligned} \frac{247.2}{0.00141} &= 175,326.45 \text{ cm}^3/\text{hr.} \\ &= 6.19 \text{ ft}^3/\text{hr. at } 25 \text{ }^\circ\text{C and atmospheric pressure} \end{aligned}$$

In all the runs,, the air supplied was set at 0.6 ft³/hr. at reactor conditions, that is for a case where T = 200 °C and P = 2,200 psig:

$$0.6 \times \frac{298}{473} \times \frac{2215}{14.7} = 56.95 \text{ ft}^3/\text{hr. at } 25 \text{ }^\circ\text{C and } 14.7 \text{ psig}$$

The comparison of the above two figures, shows that the actual air flow rate is set to be considerably higher than the theoretical flow rate needed for complete oxidation and there was always a large percentage of excess air involved for all runs.

III. Calibration of Chromatograph

The calibration was done by using three calibration solutions, #1, #2, and #3. The chromatograph was left on at all times to ensure that it was operating at steady-state condition. The operating conditions were:

| | |
|--------------------------|---------------------|
| Column temperature | 142 °C |
| Detector temperature | 206 °C |
| Injector temperature | 210 °C |
| Range | 10^{-11} Amp/m.V. |
| Attenuation | 16 |
| Chart speed | 12 in/min. |
| Air flow rate | 400 ml/min. |
| He flow rate | 20 ml/min. |
| H ₂ flow rate | 20 ml/min. |
| Air pressure | 20.21 psig |
| He pressure | 48.49 psig |
| H ₂ pressure | 12 psig |

Results of one injection:

| | |
|---------------------------------------|-------------------------------|
| Concentration of calibration solution | = 1033.95 mg/l |
| Sample volume | = 2×10^{-6} lit. |
| Weight of phenol | = 2×10^{-6} x 1033.5 |
| | = 2.0679×10^{-3} mg |

| | |
|------------------------------|--|
| Phenol peak weight | = 0.06325 gm |
| Standardization value (S.V.) | = $\frac{\text{Phenol Weight (gm)}}{\text{Peak weight of paper (gm)}}$ |
| | = 3.270×10^{-5} gm phenol/gm paper |

Tables 11, 12 and 13 show the details of analysis on the three calibration solutions.

Solution #1 was made of phenol crystals and distilled water with the concentration of 1033.95 mg/l. The attenuation for analysis was 16.

Solution #2 was a standard phenol solution 1000 mg/l. from Harleco, Phila, Pa. supplied by Canadian Laboratory Supplies Limited. Here the attenuation of 16 was used on the chromatograph.

Solution #3 was also made of phenol crystals and distilled water with the concentration of 413.2 mg/l. The attenuation of 8 was used for this case and the S.V. values obtained was multiplied by 1/2 to bring it to attenuation 16.

The Standardization Value obtained using the purchased standard solution (#2), was not in good agreement with S.V. obtained from the laboratory made solutions. It was decided to use the average S.V. of solutions #1 and #3, $S.V._{av.} = 3.31973 \times 10^{-5}$ gm phenol/gm paper for phenol analysis. In cases where different attenuation were used, the S.V. was multiplied by the ratio of new attenuation to 16.

The above procedure was followed for time when a new paper was used in the recorder. The new average S.V. thus obtained was $S.V. = 3.32094 \times 10^{-5}$ gm phenol/gm paper.

Table 11.

Calibration solution #1 1033.95 mg/l

| Sample No. | Sample Volume ⁻⁶ (litersx10 ⁻⁶) | Peak Weight (gm) | Phenol Weight _g (gm x 10 ⁻⁵) | S.V. (gm phenol/gm paper) |
|------------|---|---------------------|--|------------------------------|
| 1 | 1.2 | 0.03745 | 1240.74 | 3.313x10 ⁻⁵ |
| 2 | 1.2 | 0.03725 | 1240.74 | 3.331x10 ⁻⁵ |
| 3 | 1.2 | 0.03495 | 1240.74 | 3.550x10 ⁻⁵ |
| 4 | 2.0 | 0.06185 | 2067.90 | 3.375x10 ⁻⁵ |
| 5 | 2.0 | 0.06325 | 2067.90 | 3.270x10 ⁻⁵ |
| 6 | 2.0 | 0.06195 | 2067.90 | 3.338x10 ⁻⁵ |
| 7 | 2.0 | 0.06235 | 2067.90 | 3.285x10 ⁻⁵ |
| 8 | 2.0 | 0.06380 | 2067.90 | 3.241x10 ⁻⁵ |
| 9 | 2.0 | 0.06155 | 2067.90 | 3.360x10 ⁻⁵ |

$$S.V._{av.} = 3.34033 \times 10^{-5} \text{ gm phenol/gm paper}$$

$$\text{Standard Deviation} = 8.96 \times 10^{-7}$$

Table 12

Calibration solution #2 1000 mg/l

| Sample No. | Sample Volume ⁻⁶ (litersx10 ⁻⁶) | Peak Weight (gm) | Phenol Weight _g (gm x 10 ⁻⁵) | S.V. (gm phenol/gm paper) |
|------------|---|---------------------|--|------------------------------|
| 1 | 2.0 | 0.06375 | 2000.0 | 3.137x10 ⁻⁵ |
| 2 | 2.0 | 0.06495 | 2000.0 | 3.079x10 ⁻⁵ |
| 3 | 2.0 | 0.06615 | 2000.0 | 3.083x10 ⁻⁵ |
| 4 | 2.0 | 0.06295 | 2000.0 | 3.177x10 ⁻⁵ |
| 5 | 2.0 | 0.06345 | 2000.0 | 3.152x10 ⁻⁵ |
| 6 | 2.0 | 0.06410 | 2000.0 | 3.120x10 ⁻⁵ |
| 7 | 2.0 | 0.06600 | 2000.0 | 3.030x10 ⁻⁵ |
| 8 | 2.0 | 0.06365 | 2000.0 | 3.142x10 ⁻⁵ |
| 9 | 2.0 | 0.06365 | 2000.0 | 3.142x10 ⁻⁵ |

$$S.V._{av.} = 3.11133 \times 10^{-5} \text{ gm phenol/gm paper}$$

$$\text{Standard Deviation} = 5.48 \times 10^{-7}$$

Table 13

Calibration solution #3 431.2 mg/l

| Sample No. | Sample Volume (liters $\times 10^{-6}$) | Peak Weight (gm) | Phenol Weight (gm $\times 10^{-5}$) | S.V. (gm phenol/gm paper) |
|------------|---|---------------------|---|------------------------------|
| 1 | 2.0 | 0.04970 | 862.4 | 3.470×10^{-5} |
| 2 | 2.0 | 0.05355 | 862.4 | 3.233×10^{-5} |
| 3 | 2.0 | 0.05155 | 862.4 | 3.346×10^{-5} |
| 4 | 2.0 | 0.05525 | 862.4 | 3.122×10^{-5} |
| 5 | 2.0 | 0.05380 | 862.4 | 3.206×10^{-5} |
| 6 | 2.0 | 0.05180 | 862.4 | 3.330×10^{-5} |
| 7 | 2.0 | 0.05100 | 862.4 | 3.382×10^{-5} |
| 8 | 2.0 | 0.05220 | 862.4 | 3.304×10^{-5} |

$$S.V._{av.} = 3.29912 \times 10^{-5} \text{ gm phenol/gm paper}$$

$$\text{Standard Deviation} = 1.093 \times 10^{-6}$$

IV. Phenol Analysis

The phenol peaks on the chromatograms were cut and weighed. Standardization Value was used to determine the phenol concentration in the samples the followings are the results for one injection in run #32

| | | |
|--------------------|----------------------|--------|
| Feed concentration | 4449.41 | mg/l |
| Liquid feed rate | 8200 | ml/hr. |
| Sample volume | 1.8×10^{-6} | ml |
| Peak weight | 0.06590 | gm |

and thus:

$$\begin{aligned} \text{Phenol concentration} &= \frac{\text{Peak Weight}}{\text{Sample volume}} \times \text{S.V.} \\ &= 1215.83 \quad \text{mg/l} \end{aligned}$$

The average concentration for the effluent samples was found to be 1748.23 mg/l for above run after it was corrected for reactor conditions.

V. Phenol Conversion

The percentage phenol conversion is calculated as:

$$\text{percentage conversion} = \frac{\Delta C_{\text{Ph}}}{C_{\text{Ph}(0)}} \times 100$$

and for the above run it was found to be:

$$\begin{aligned} \text{conversion} &= \frac{4449.41 - 1748.73}{4449.41} \times 100 \\ &= 60.71\% \end{aligned}$$

VI. Reaction Rate

The rate of reaction is calculated based on the unit volume of the reactor. For the above run:

$$\begin{aligned} \text{Phenol flow in} &= 4449.41 \times 8.2 \\ &= 36485.16 \quad \text{mg/hr.} \\ &= 0.388140 \quad \text{gm mole/hr.} \end{aligned}$$

$$\begin{aligned} \text{Phenol flow out} &= 1748.23 \cdot 8.2 \\ &= 0.152505 \quad \text{gm mole/hr.} \\ \text{Reactor volume} &= 3.648 \quad \text{l} \end{aligned}$$

and

$$\begin{aligned} \text{Reaction Rate} &= \left(\frac{dN_{\text{Ph}}}{dt} \right) \frac{1}{V_R} \\ &= \frac{0.38814 - 0.152505}{3.648} \\ &= 0.06459 \quad \text{gm moles/hr.l} \end{aligned}$$

VII. Calculation of Gas-Liquid Holdup Ratio

Assuming that gas phase in the reactor is saturated with liquid and behaves as an ideal gas, the gas holdup ratios can be calculated as follows by the previously described method of measuring the volume of liquid water collected in the graduated cylinder (L) at room temperature and correcting this volume for the actual conditions inside the reactor. To do this a mass balance around the reactor is written as:

$$L \cdot \rho_{25} = V_L \cdot \rho_T + \text{grams water in gas phase}$$

where

$$\begin{aligned} \text{grams water in gas} &= N_w \cdot 18 \\ &= \frac{P_w V_G}{RT} \cdot 18 \end{aligned}$$

and

$$V_G = V_R - V_L$$

then:

$$L \times \rho_{25} = V_L \times \rho_T + \frac{18 p_w}{RT} (V_R - V_L)$$

solving this for V_L gives:

$$V_L = \frac{L \left(\frac{\rho_{25}}{\rho_T} \right) - \alpha V_R}{1 - \alpha}$$

(5)

with

$$\alpha = \frac{18 p_w}{RT \rho_T}$$

In table (14) the values of V_L are listed for different values of L , at temperatures of 25, 70, 120, and 200 °C. It can be seen from this table that the volumes which are not corrected for actual temperatures could bring errors of high magnitudes. This error can easily be out of the range of holdup change due to change in variable within which the holdups have been studied.

Table 14

Corrected Liquid Volumes in Reactor

| L (ml) | V_L (ml) | | | |
|-----------------|------------|---------|---------|----------|
| | T = 25 °C | 70 °C | 120 °C | 200 °C |
| 2400 | 2399.97 | 2447.72 | 2542.31 | 2772.54 |
| 2600 | 2599.98 | 2651.77 | 2754.63 | 3007.62 |
| 2800 | 2799.98 | 2855.82 | 2966.96 | 3242.69 |
| 3000 | 2999.98 | 3059.86 | 3179.28 | 3477.77 |
| 3200 | 3199.99 | 3263.91 | 3391.61 | *3712.85 |
| 3400 | 3399.99 | 3467.96 | 3603.93 | *3947.92 |

*The values exceeding the reactor volume.

VIII. Calculation of Liquid Residence Time

The calculations are made based on the gas holdup ratios obtained experimentally. Here the calculation is given for run =19, 20 and 21 with

Liquid flow = 6000 ml/hr.

Temperature = 200 °C

Pressure = 800, 1500, 2200 psig

Air flow rate= 0.6 ft³/hr. at conditions

From Figure 5 the gas holdup would be the same for 25 ° and 200 °C. Also Figure 6 shows that the change of holdup is negligible for this wide range of pressure and holdup can be assumed 20% for above conditions but a liquid flow rate of 4,000 ml/hr. Meanwhile from Figure 3, the change in holdup due to change in liquid flow from 4,000 to 6,000 ml/hr. is also not considerable and the gas holdup can be assumed to be 20% for these runs. Then:

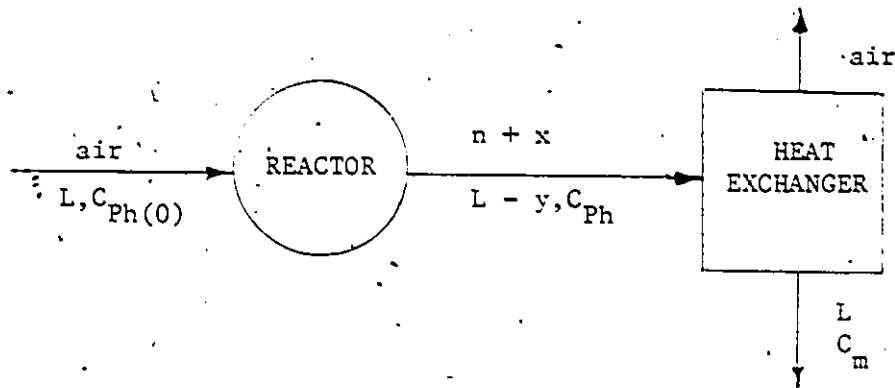
$$\begin{aligned} V_L &= 0.8 V_R \\ &= 0.8 \times 3648 \\ &= 2918.4 \text{ ml.} \end{aligned}$$

and

$$\begin{aligned} \text{Liquid Residence Time} = \tau &= \frac{V_L}{L \cdot \text{Flow}} \\ \tau &= \frac{2918.4}{6000} \\ &= 0.486 \text{ hr.} \end{aligned}$$

IX. Calculation of Reactor Concentration

Actual phenol concentration in reactor exit line would not be necessarily the same as the measured concentration of samples collected in the separator. This comes from the fact that the liquid leaving the reactor will contain some water condensed from the gas phase while passing through heat exchanger. For relating the reactor concentration (C_{PH}) to the measured phenol concentration (C_m) a mass balance around the heat exchanger can be written as follows:



Assuming the same air flow rate is flowing through the system and the amount of phenol vapor in reactor exit gas and the separator, is negligible compared to that in the liquid phase, then

$$(L - y)C_{Ph} = L \cdot C_m$$

or

$$C_{Ph} = C_m \left(\frac{1}{1 - \frac{y}{L}} \right)$$

but

$$y = \frac{18 \cdot sx}{1000 \cdot \rho_T}$$

and

$$x = N_{\text{air}} \cdot \frac{P_w}{P - p_w}$$

where

$$N_{\text{air}} = \frac{P \cdot V_{\text{air}}}{RT}$$

then:

$$C_{\text{Ph}} = C_m \left(\frac{1}{1 - \frac{1S}{1000} \cdot \frac{s}{\rho_T} \cdot \frac{P \cdot 0.6 \cdot 28.316}{RT} \cdot \frac{P_w}{P - P_w} \cdot \frac{1}{L}} \right)$$

$$= C_m \cdot \beta$$

The concentration correction factor (β) can be calculated for the conditions of each experimental run by using the above equation. Values for β are presented in Table 15 where the degree of saturation was assumed to be 85 percent except for cases at 250 °C and pressures of 800 and 1500 psig where it was assumed to be 44 and 75 percent respectively.

As can be seen from Table 15 the highest correction factor used in this work was 1.0894 which makes the C_{Ph} be about 9% more than C_m and the average difference is about 5%. These factors are used to correct all concentrations to give reactor concentrations.

Table 15

Values of Concentration Correction Factor (β)
at Different Conditions

| L ml/hr. | T = 200 °C | | | T = 250 °C | | |
|-------------|-----------------|--------------|--------------|-------------|--------------|--------------|
| | P = 800 psig | 1500 psig | 2200 psig | 800 psig | 1500 psig | 2200 psig |
| 2000 | 1.0894 | 1.0750 | 1.0708 | 1.3583 | 1.2703 | 1.2531 |
| 4000 | 1.0428 | 1.0361 | 1.0342 | 1.1519 | 1.1190 | 1.1123 |
| 6000 | 1.0281 | 1.0239 | 1.0225 | 1.0964 | 1.0763 | 1.0722 |
| 8000 | 1.0209 | 1.0178 | 1.0168 | 1.0706 | 1.0562 | 1.0532 |

X. Calculation of "Maximum" Air Flow Rate

Based on results of analysis on the gas phase, for any liquid feed rate there exists an air flow rate beyond which all the liquid would be taken into gas phase and thus create undesirable condition for WAO. The "Maximum" air flow rate for run #23 is calculated to be 7.18 ft³/hr.

Temperature 200 °C
 Pressure 800 psig or
 55.42 atm.
 Liquid flow rate 2000 ml/hr.

It can be written:

$$x = N_{\text{air}} \cdot \frac{\bar{p}_w}{P - \bar{p}_w}$$

and also

$$x = \frac{L \cdot \rho_{25}}{18} \quad \text{if the gas is saturated}$$

also

$$N_{\text{air}} = \frac{P \cdot V_{\text{air}}}{RT}$$

then:

$$\begin{aligned} V_{\text{air}} &= \frac{L \cdot \rho_{25} \cdot R \cdot T \cdot (P - \bar{p}_w)}{18 \cdot P \cdot \bar{p}_w} \\ &= \frac{2000 \cdot 0.977 \cdot 0.08206 \cdot 473 \cdot (815 - 225)}{18 \cdot \frac{815}{14.7} \cdot 225} \\ &= 203.36 \quad \text{liters/hr.} \\ &= 7.18 \quad \text{ft}^3/\text{hr.} \end{aligned}$$

Thus the rate of 0.6 ft³/hr. which was actually used was far less than the amount needed to deplete all the liquid in reactor.

XI. Dependency of Rate of Reaction on Temperature

From the Arrhenius Law:

$$k_r \propto e^{-E/RT}$$

then

$$\begin{aligned} \frac{(\text{Rate})_{250}}{(\text{Rate})_{200}} &= \frac{(k_r)_{250}}{(k_r)_{200}} = \frac{e^{-E/R(523)}}{e^{-E/R(473)}} \\ &= e^{\frac{E}{R} \left(\frac{1}{473} - \frac{1}{523} \right)} \end{aligned}$$

assuming $E = 11,000^{30}$ cal/mole the theoretical value for the ratio of rate constants is:

$$\frac{(\text{Rate})_{250}}{(\text{Rate})_{200}} = 3.07$$

From the experimental data for runs at 200 and 250 °C with other conditions being the same we have:

$$\frac{(\text{Rate})_{250}}{(\text{Rate})_{200}} = \frac{(\text{Conversion})_{250}}{(\text{Conversion})_{200}} = 1.16$$

Thus the experimental values show that the overall rate of reaction increased almost one third of the case where the overall rate is controlled by chemical reaction.

APPENDIX 4. Steps-In-Series Reaction Control Mechanism

Assuming a combined effect of mass transfer and chemical reaction controls the overall rate of reaction where the liquid phase resistance and chemical reaction act in series on the overall rate of reaction, for steady-state operation, the overall rate would be equal to each of the mass transfer and chemical reaction rates. The rate of mass transfer of oxygen through the bubble-liquid interface can be expressed²⁹ as:

$$\frac{\text{Moles of } O_2 \text{ transferred}}{\text{hr.}} = k_1 \cdot a \cdot V_R (C^* - C_{O_2})$$

where k_1 is a mass transfer coefficient, a is the bubble surface area per unit reactor volume (V_R), and C^* and C_{O_2} are the saturation and actual oxygen concentration in the liquid respectively.

The rate of chemical reaction is:

$$\frac{\text{Moles of phenol reacted}}{\text{hr.}} = k_R \cdot V_R \cdot C_{O_2}^m \cdot C_{Ph}^n$$

where K_R is the reaction rate constant, C_{Ph} is the reactor phenol concentration, and m and n are exponents. Also for a steady-state condition:

$$b \frac{\text{moles of } O_2 \text{ transferred}}{\text{hr.}} = \frac{\text{moles phenol reacted}}{\text{hr.}}$$

where b is the stoichiometric ratio of moles of phenol to moles of oxygen. Then the overall rate of reaction (r) would be:

$$r = k_r \cdot V_R \cdot C_{O_2}^m \cdot C_{Ph}^n$$

and
$$= k_1 \cdot a \cdot b \cdot V_R (C^* - C_{O_2})$$

and also
$$= L \cdot \Delta C_{Ph}$$

where L is the liquid feed rate and ΔC_{Ph} is the concentration change of phenols in the reactor. Also for a gas holdup ratio of 20%:

$$\tau = \frac{V_L}{L} = \frac{0.8 V_R}{L}$$

where τ and V_L are the residence time and the volume of liquid in the reactor respectively.

Eliminating the C_{O_2} between the two rate equations and combining it with other equations above will result in the following equation:

$$\Delta C_{Ph} = \frac{\tau}{0.8} k_r (C^* - \frac{0.8 \Delta C_{Ph}}{k_1 \cdot a \cdot b \cdot \tau})^m \cdot C_{Ph}^n$$

But according to Henry's Law: $C^* = \frac{P_{O_2}}{H}$, while the partial pressure of oxygen can be written as:

$$P_{O_2} = 0.21(P - \bar{p}_w)$$

where the air is assumed to have 21 mole% oxygen, and s is the degree of saturation and is taken to be 85 percent based on experimental results, and \bar{p}_w is the partial pressure of water in the reactor. Thus the phenol conversion is:

$$\begin{aligned} \text{Conversion} &= \frac{\Delta C_{\text{Ph}}}{C_{\text{Ph}}(0)} \\ &= \frac{\tau}{0.8 C_{\text{Ph}}(0)} k_r \cdot C_{\text{Ph}}^n \left(\frac{0.21(P - 0.85\bar{p}_w)}{H} - \frac{0.8\Delta C_{\text{Ph}}}{k_{\text{L.a.b.}\tau}} \right)^m \quad (6) \end{aligned}$$

For obtaining estimated values for m , n , k_r , and $k_{\text{L.a}}$ the above model is fitted to the experimental data using a computer program which is presented in the following pages with these notations:

y = conversion

$$X(1) = \frac{\tau}{0.8 C_{\text{Ph}}(0)}$$

$$X(2) = C_{\text{Ph}}$$

$$X(3) = (0.21(P - 0.85\bar{p}_w))/H$$

$$X(4) = (0.8 \Delta C_{\text{Ph}})/(b.\tau)$$

$$\theta(1) = k_r$$

$$\theta(2) = n$$

$$\theta(3) = k_{\text{L.a}}$$

$$\theta(4) = m$$

and

$$y = X(1) \cdot \theta(1) \cdot X(2) \left[X(3) - \frac{X(4)}{\theta(3)} \right]^{\theta(2)} \theta(4)$$

