The direct vapour-phase oxidation of benzene to phenol

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THE DIRECT VAPOUR PHASE OXIDATION
OF BENZENE TO PHENOL

by

U. K. BUTTA

**

A thesis submitted for the degree of Doctor of Philosophy of Loughborough University of Technology

**

Supervisor: J. Glover

Department of Chemical Engineering

November 1969
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SUMMARY

The homogeneous gas phase oxidation of benzene to phenol with air has been studied with the objective of finding the economically optimum conditions for a commercial process for the production of phenol. The experimental work was carried out in the temperature range of 585°C to 650°C, reaction times of 0.4 to 1.2 seconds, and at a total pressure of one atmosphere. Most of the experiments were carried out in a quartz lined reactor.

It was found that benzene (less than 0.1% impurities) gave lower selectivities for phenol than Analar benzene which contained 0.3 to 0.5% impurities. The effect of a homogeneous promoter (chloroform) on the oxidation reaction was also studied.

The experimental results were correlated both by means of a free radical mechanism and semi-empirical rate equations. The results confirm previous findings that the initiation step is probably the production of a phenyl radical from benzene, and a major termination reaction is the recombination of phenyl radicals to produce diphenyl.

The kinetic data used in a plant design to produce phenol by oxidation of benzene with air or oxygen and an optimization procedure was used to find the economically optimum conditions.

The optimum conditions in the region of experimental data (0.8% phenol yield at 69% selectivity) would produce phenol at a cost of about £61/ton, based on benzene at £25/ton which is unlikely to be commercially attractive.

However, an extrapolation of the experimental data using the kinetic model indicated that at 565°C and contact time of 6 seconds, the yield of phenol would be 1.3% with a selectivity of 79% leading to a phenol price of £47/ton which may possibly be commercially attractive.
CHAPTER 1

Introduction and Preliminary Investigation
CHAPTER 1

Introduction and Preliminary Investigations

Phenol has been a commercial bulk chemical since 1875. Initially, the bulk of the demand was satisfied from natural resources, but spectacular growth in its demand with diversification of its uses resulted in the development of synthetic routes to phenol. At present, six commercially exploited processes of phenol synthesis are operating. Dr Prahl, (1), innovator of the benzene sulfonation process, once commented:

'The seemingly simple introduction of a hydroxyl group to benzene has led to such a number of processes, that there is probably no other example of such a variety of methods of converting the same simple substance to the same simple product.'

Two new processes (cyclohexane oxidation and toluene oxidation) have come into being since he made that comment.

The investigations on a new route to phenol - the direct vapour phase oxidation of benzene with air or oxygen - induced by high temperature (500-700°C) are presented in this report. A typical commercial process development strategy has been employed in the present study, with economic evaluation and economic optimisation of the process, along with investigations on the mechanism and kinetics of the process. The whole approach is summarised in Fig. 1.01.

1.1 Technical and Economic Aspects of Phenol processes and the Need for an Alternative Route:

The main features of the six commercial processes (2, 3, 4) are outlined in Fig. 1.02 and Table 1.01. The sulfonation and the chlorobenzene processes are the oldest ones, and of diminishing importance. The cumene oxidation process produces 43% and the Raschig process produces 19% (Table 1.01) of the total production in the US. No clear
Fig. 1.01
The Scheme for the Investigation of the Direct Vapour Phase Oxidation Process

1. Literature Survey
   - Preliminary evaluation of economically optimum conditions for direct vapour phase oxidation
   - Economically attractive region of process conditions

2. Experimental work in the economically attractive regions

3. Reaction Mechanism and kinetic model

4. Economic optimisation based on the kinetic model
   - Optimum process conditions
picture of the commercial viability of the two new processes (cyclohexane and toluene oxidation) has emerged yet.

The economics of the processes are presented in Table 1.02 on the basis of uniform unit costs of the component factors. The cost data used in Table 1.02 and elsewhere in the present work are presented in Appendix I. The appropriate cost index has been used to convert all the data to 1968 cost level.

The sulfonation process has a very high raw material cost and depends on realizing a substantial by-product credit for the large quantities of sodium sulfite and sulfate produced. According to K. C. Banciu (5), no new sulfonation plants are likely to be built, but amortized plants or plants integrated with sulfate pulp manufacture will continue to operate usefully for a little longer.

The chlorobenzene process also has high raw material costs and presents corrosion difficulties. The cost of phenol by this process at £83.8/ton is on the same level as that of the sulfonation process and is not competitive with other processes (Table 1.02). It can, however, still be a contender in the case of large units integrated with caustic soda - chlorine complex and availability of cheap power for chlorine production.

The Hooker-Raschig process has the advantage of having a single product and hence is not dependent on any by-product credit. The main disadvantage of this process is its high investment cost (6) expressed by the relationship (year 1963):

$$L = 4627 \times (capacity, \text{Tons/year})^{0.60} \quad (i).$$

A cost of phenol versus capacity plot on the basis of the above equation and the data in Table 1.02 and Appendix I is presented in Fig. 1.03. It is seen from Fig. 1.03 that to be competitive, a plant based on the Hooker-Raschig process has to have a capacity greater than 30,000 tons/year.
Fig. 1.02

Processes for Phenol Manufacture
<table>
<thead>
<tr>
<th>Process</th>
<th>Sulfonation</th>
<th>Chlorobenzene</th>
<th>Hooker- Raschig</th>
<th>Cumene</th>
<th>Toluene</th>
<th>Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Licensor</td>
<td>Dow Chemical Co.</td>
<td>Hooker Chemical Co.</td>
<td>Dow Chemical Co.</td>
<td>Scientific Design Co.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Share in total U.S. Production</td>
<td>16</td>
<td>18</td>
<td>19</td>
<td>43</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>Tons of Raw Material per ton of Phenol:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>.9</td>
<td>.9</td>
<td>1.0</td>
<td>1.1</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>Toluene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(1.5 ton of Cumene)</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Propylene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HCL</td>
<td>-</td>
<td>.5</td>
<td>.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Caustic Soda</td>
<td>1.5</td>
<td>1.2 tons</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chlorine</td>
<td>-</td>
<td>.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Air</td>
<td>-</td>
<td>-</td>
<td>2.2</td>
<td>10,000 cft</td>
<td>34,000 scf</td>
<td>20,000 cft</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>Small</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TOTAL</td>
<td>3.9</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>By-products</td>
<td>Sodium Sulfite</td>
<td>Sodium Sulfate</td>
<td>Poly- Chlorobenzene</td>
<td>None</td>
<td>Acetone = 0.6 ton</td>
<td>Benzoic Acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hydrogen</td>
</tr>
</tbody>
</table>
### TABLE 1.02
Economics of Phenol Production* (20,000 T/a)

<table>
<thead>
<tr>
<th>Process</th>
<th>Sulfonation</th>
<th>Chlorobenzene</th>
<th>Hooker-Raschig</th>
<th>Cumene*</th>
<th>Toluene</th>
<th>Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment</td>
<td>1.5</td>
<td>1.5</td>
<td>2.00</td>
<td>1.5</td>
<td>2.9</td>
<td>1.5</td>
</tr>
<tr>
<td>£/ton-year Phenol</td>
<td>75</td>
<td>75</td>
<td>100</td>
<td>75</td>
<td>145</td>
<td>75</td>
</tr>
<tr>
<td>Production Cost per ton Phenol</td>
<td>£/ton</td>
<td>% on Cost</td>
<td>£/ton</td>
<td>% on Cost</td>
<td>£/ton</td>
<td>% on Cost</td>
</tr>
<tr>
<td>Raw Material</td>
<td>67.0</td>
<td>66.6</td>
<td>70.0</td>
<td>67.0</td>
<td>35.3</td>
<td>52.8</td>
</tr>
<tr>
<td>Utilities</td>
<td>10.3</td>
<td>13.4</td>
<td>11.5</td>
<td>10.5</td>
<td>16.0</td>
<td>11.6</td>
</tr>
<tr>
<td>Catalyst/Chemicals</td>
<td>2.4</td>
<td>1.5</td>
<td>1.4</td>
<td>1.9</td>
<td>4.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Labour/Maintenance</td>
<td>7.9</td>
<td>7.9</td>
<td>8.5</td>
<td>7.9</td>
<td>9.6</td>
<td>8.0</td>
</tr>
<tr>
<td>Depreciation/Interest</td>
<td>11.2</td>
<td>11.5</td>
<td>11.2</td>
<td>9.5</td>
<td>11.2</td>
<td>16.8</td>
</tr>
<tr>
<td>TOTAL</td>
<td>96.8</td>
<td>104.0</td>
<td>61.5</td>
<td>66.6</td>
<td>77.3</td>
<td>68.8</td>
</tr>
<tr>
<td>By-product Credit</td>
<td>14.2</td>
<td>15.0</td>
<td>15.2</td>
<td>14.8</td>
<td>18.0</td>
<td>26.9</td>
</tr>
<tr>
<td>Production Cost</td>
<td>84.6</td>
<td>88.8</td>
<td>61.5</td>
<td>48.8</td>
<td>77.3</td>
<td>64.3</td>
</tr>
</tbody>
</table>

* Propylene - £30/ton
H₂ - £75/ton
Benzene - £25/ton
few other disadvantages of the process are high power consumption and chloride corrosion.

When the first cumene process came into being, no hindrance to its growth was foreseen. The profitability of the process depends heavily on the by-product credit from acetone (Fig. 1.03), 0.6 ton of which is formed per ton of phenol produced. The market conditions in the fifties, when the process became established, made the acetone credit an advantage for the process. But presently, this process does not appear to be so attractive, mainly because of setback and instability in the acetone price and demand (7, 8). The by-product problems have often resulted in phenol plants running at reduced capacity in the sixties (7). At 20,000 tons/year capacity and an acetone price of £30/ton, the cumene oxidation process breaks even with a Hooker-Raschig process of 30,000 tons/year capacity.

Among the newer processes, the cyclohexane oxidation process appeared to be very attractive from its evaluation in the literature (9, 10). When benzene is used as starting material, the total hydrogen requirement for benzene hydrogenation and cyclohexanone hydrogenation (to cyclohexanol) exceeds the amount of hydrogen generated in the cyclohexanol dehydrogenation to phenol (Fig. 1.02). When just cyclohexane is used as starting material, the net back from hydrogen produced in the dehydrogenation becomes an important factor in the economics.

In other words, minimisation of the formation of cyclohexane, or maximising the selectivity of cyclohexanol in the oxidation step, is the crucial factor in the economics of the process. A cyclohexanol selectivity of 90% and above is regarded as essential for the competitiveness of the process, and such selectivities are reported to have been achieved by the recently developed processes (10).

However, Monsanto's first plant based on this process closed down
Fig. 1.03a
Phenol Production Cost for Raschig Process (6)

Fig. 1.03b
Cumene Oxidation Process Economics - the Dependance of Phenol Production Cost on Acetone Credit (8)
recently for economic reasons (12). Possibly the high yields claimed in pilot plant studies did not actually materialise. Analysing the situation, ECN (12) concluded that cyclohexane based phenol 'could be competitive as an adjunct to really large cyclohexane oxidation plants producing caprolactum or adipic acid.'

Little is known about the economics of the toluene oxidation process. However, assessing this process, ECN (13) observed that one of Dow Chemical Company's reasons for undertaking development of the process was greater abundance and lack of uses making toluene a cheaper source. But in recent years, with the production of benzene by hydrodealkylation of toluene at a cost of about £6/ton, benzene could have a ceiling price consisting of toluene's alternative value as an octane improver plus the hydrodealkylation cost. The cost of phenol on this basis, presented in Table 1.02, does not make the process more attractive than the Hooker-Raschig or the cumene process.

In Table 1.02, cumene oxidation with phenol at a cost of £45.7/ton looks most attractive, provided full by-product credit is obtained. Information on phenol plants being built at present (14) shows this process to be still the most favoured one.

1.2 The Direct Oxidation of Benzene to Phenol:

The major shortcomings of the existing processes discussed above can be summarised as follows:

(1) High raw material cost (sulfonation, chlorination)
(2) Dependence on substantial by-product credit (cumene, sulfonation, cyclohexane)
(3) High investment due to process complexity (Hooker-Raschig)

These shortcomings can be mainly attributed to the indirect processes used for attaching an OH group to the benzene ring. Obviously, the
direct oxidation route is the simplest (Fig. 1.01) and could possibly eliminate some or all of the above problems. Consequently, the direct oxidation route to phenol has attracted considerable attention. A number of different direct oxidation techniques have been used to study the conversion of benzene to phenol. Table 1.03 summarises the main features of the various investigations.

**TABLE 1.03**

Methods of Direct Oxidation of Benzene

<table>
<thead>
<tr>
<th>Process</th>
<th>Process Conditions</th>
<th>Benzene Conversion</th>
<th>Phenol Selectivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour phase oxidation with solid supported catalysts</td>
<td>300-500°C</td>
<td>up to 3%</td>
<td>20-30%</td>
<td>15, 16, 17 18</td>
</tr>
<tr>
<td>Liquid phase oxidation</td>
<td>-</td>
<td>1%</td>
<td>-</td>
<td>23, 24</td>
</tr>
<tr>
<td>Thermal and radiation oxidation in aqueous solution in presence of metal ions</td>
<td>20-200°C 30 atm Y or X-rays ultra violet rays etc.</td>
<td>5-6%</td>
<td>30-40%</td>
<td>25, 26, 27 28, 29, 30 31, 32, 33</td>
</tr>
<tr>
<td>Oxidation under electric discharge</td>
<td>vacuum room temperature</td>
<td>2-15%</td>
<td>not reported</td>
<td>34, 35, 36 37</td>
</tr>
<tr>
<td>Homogeneous vapour phase oxidation (thermal) with oxygen/air</td>
<td>350-700°C</td>
<td>up to 35%</td>
<td>20-30% up to 60% (mole) reported</td>
<td>38, 63-78</td>
</tr>
</tbody>
</table>

1.2.1 **Vapour Phase Oxidation with Solid Supported Catalysts:**

The work of J. Weiss and C. R. Downs (15), using a wide range of metal and metal oxide catalysts produced very discouraging results, with hardly more than 1-2% phenol yield, the main products being maleic acid, diphenyl, benzoquinone and carbon oxides. The negative influence of metal oxide catalysts on phenol formation has been emphasised by R. E. Marek (19). According to C. A. Coulson (20) and C. H. Schleshman (21), preferential adsorption of phenol takes place on the catalyst
surface due to its polarity. D. E. Eley (22) found from the calculation of heat of chemisorption that benzene is weakly chemisorbed at the metal surface of the catalyst.

Recently, however, Y. Manabe et al (16) and K. Hosaka et al (17) have obtained better results (3-4% yield of phenol) using $H_3PO_4$ celite - or vanadium catalysts. However, the phenol selectivity (20-40%) has been low in all cases. Mobil Oil (18) is reported to have developed an alumino-silicate-rare earth catalyst for the purpose.

1.2.3 Liquid Phase Oxidation:

The limited number of investigations carried out in this field have not proved to be very successful. Simonds and McArthur (23) studied a batch process in a copper bomb at 300-1,000 psi with pure oxygen and an HF catalyst. They reported high selectivity for phenol (60-100%) but very low conversions (.1-.2%). Standard Oil has patented a liquid phase process using an HF-BF$_3$ catalyst (24).

1.2.4 Thermal and Radiation Oxidation in Aqueous Solution of Metal Salts

A considerable amount of work on the oxidation of benzene induced thermally or by radiation in aqueous solution of metal salts has been reported (25-33). R. Danno (25) has made a review of developments in this field with extensive references. At 150-200°C metal ions facilitate the production of OH radicals by the type of reaction:

$$Fe^{2+} + O_2 + H^+ \rightarrow Fe^{3+} + HO_2^\cdot$$

$$Fe^{2+} + HO_2^\cdot + H^+ \rightarrow Fe^{3+} + H_2O_2$$

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{++} + .OH$$

The .OH radical takes part in phenol formation, being relatively stable up to 200°C. Radiation by $\gamma$-rays, X-rays or ultra-violet facilitates the break-up of water into .OH radicals -

$$H_2O \rightarrow .OH + H^+$$
and phenol forming reactions take place at 150-200°C. Typical yields of phenol are reported in Table 1.04. The main products are phenol, diphenyl, p-ter-phenyl, catechol, hydroquinone and fatty acids.

**TABLE 1.04**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Radiation</th>
<th>Thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.1</td>
<td>0.1</td>
</tr>
<tr>
<td>150</td>
<td>5.5</td>
<td>0.2</td>
</tr>
<tr>
<td>175</td>
<td>22.0</td>
<td>0.8</td>
</tr>
<tr>
<td>200</td>
<td>25.1</td>
<td>23.0</td>
</tr>
</tbody>
</table>

* Selectivities reported: 30-50%

Although fundamental studies on radiation chemistry are progressing rapidly, the cost of the radiation energy is very high and it has been exploited commercially for production of bulk chemicals in very few cases (e.g. Esso alkyl sulfonate process).

1.2.5 Oxidation in Electric Discharge

Oxidation in electric discharge in the presence of rarefied oxygen (34, 35, 36, 37), like radiation oxidation, does not appear to be attractive for commercial process development. Lemetre and Caprara (38) have estimated from literature data that the power requirement per kg of phenol by this process would be in the order of 150-250 kwh. At a rate of £4.5 per 1,000 kwh the power cost alone becomes over £600 per ton of phenol.

1.3 Homogeneous Thermal Oxidation in Vapour Phase with Air or Oxygen

This method, henceforth referred to as the direct vapour phase oxidation, assumes importance in view of the wide range of conversions (0-35%) and selectivities (0-60%) which have been obtained. Being a
conventional process, its economics are easier to evaluate and likely to be more attractive than the other techniques requiring costly forms of energy, even for similar conversions and selectivity.

There is little literature on the economics of phenol production by direct vapour phase oxidation of benzene. The range of operating conditions, conversion and selectivity for phenol presents an interesting problem of economic optimisation of the process. A preliminary evaluation of the process, and development of a process model for optimisation, was deemed necessary.

1.4 The Yield-Selectivity Relationship for Phenol from Vapour Phase Benzene Oxidation

Typical data from the literature (38, 70, 72) is presented in Fig. 1.04. The data shows two distinct trends.

1. Improvement of yield and selectivity of phenol by the use of organic promoter (data of Lemetre and Caprara (38));

2. Improvement of selectivity with lowering of yield of phenol.

The data of Lemetre and Caprara, which covers a wider range of yield compared to other authors, shows these two trends clearly. Their data, however, does not cover the region below 2.0% yield in the case of promoter, and .3% in the case of pure benzene. For a preliminary evaluation of the process, the data for the two cases (pure benzene and promoter) has been correlated by equations of the form:

$$\text{Selectivity} = A + \frac{B}{C + \text{Yield}} \quad (ii)$$

The value of the constants obtained by minimising the error square between calculated and given values of the variables are presented in Table 1.05.
Literature Data on the Yield and Selectivity of Phenol from the Direct Vapour Phase Oxidation of Benzene
In general it is unwise to extrapolate any empirical relation significantly beyond the last data point unless substantiated by theory. However, in the absence of any correlation based on a reaction mechanism, the use of the above relationship for preliminary evaluations can be justified on the following grounds:

1. The main products of the vapour phase oxidation of benzene are phenol, diphenyl, CO and CO₂. The formation of the oxides of carbon has been attributed by several authors to the decomposition of phenol (Chapter 2). At low yields of phenol, its decomposition is unlikely.

2. The data of Lemetre and Caprara (Appendix II) shows that lower yields and higher selectivities are obtained by lowering the temperature from 700 to 600°C. As the temperature is lowered, the phenol diphenyl ratio rises sharply, going up to 5 at 600°C which is equivalent to 84% of liquid products being phenol.

Ganeson (39) developed a simple optimisation program on the basis of a recycle flowsheet and evaluated the cost of production of phenol at various yields using a yield-selectivity relation for pure benzene.
(Curve 1, Fig. 1.04). He concluded that the optimum yield was .1%, corresponding to nearly 100% selectivity, thus stressing the importance of the study of the process at high selectivities and low conversions. However, Ganeson made some gross underestimation of capital costs, resulting in the underestimation of phenol cost at low conversions. A new process cost model was developed for economic optimisation as well as preliminary evaluation studies in order to find the economically attractive process conditions.

1.5 Preliminary Evaluation of the Direct Oxidation Process

The process cost model, developed for optimisation, is based on the flowsheet presented in Fig. 1.05. The details of the development of the cost equations are given in the section on optimisation (Chapter 7). A brief description of the process flowsheet follows. A detailed description of the flowsheet is given in Chapter 7.

1.5.1 Process Flowsheet

Vapourised benzene and air, after being pre-heated by the reactor product stream, passes into the furnace-reactor. The product stream, after heat exchange with the feed, is cooled, partially condensed, and flashed to separate phenol and diphenyl along with some benzene. The condensed liquid is fractionated to recover phenol and the benzene is recirculated. The vapours from the first separator drum are further condensed to liquefy all benzene and remove the gases in another flash drum. The benzene is recycled.

In an alternative case, pure oxygen is considered instead of air as the oxidising medium. In this case (dotted lines in Fig. 1.05), the only difference from the former scheme is after the first flash separator. Here, after separation of phenol and diphenyl, the vapours - mainly unreacted benzene and oxygen - are recirculated without further condensation by a centrifugal compressor, thus saving the cost of
Fig. 1.08
Flow Scheme for Benzene Oxidation Process
condensation and revapourisation of the unreacted benzene.

In order to prevent a build up of inerts in the system, a bleed stream of reactant vapor is withdrawn, the liquid (mainly benzene) is condensed, separated from the gases which are purged out, and recycled.

1.5.2 Cost Analysis

The process cost (details in Chapter 7) has been calculated on the following basis:

- Capacity = 20,000 tons phenol/year
- Capital cost = 4.0 x (cost of equipment)
- Operating cost = cost of benzene and utilities
- Fixed charges = 21% of capital cost
- Cost of phenol per ton = (fixed charges + operating cost)
  
  per ton phenol - by-product credit

Equipment costs, and hence the capital cost, are greatly affected by the yield of phenol which determines the recycle ratio. The cost of benzene required is dependant on the selectivity. Other factors on which the equipment specifications and overall cost depend are temperature, % oxygen in feed, pressure, etc. The economics of phenol production for a typical process conditions are given in Table 1.06.

For the present evaluation, the process variables have been taken as constant at 600°C, 1 atm and oxygen requirement of 1.5 times that of stoichiometric value for phenol formation. The cost evaluation has been made for various values of yield and selectivity. The evaluations based on the cost equations given in Chapter 7 are tabulated in Appendix I, Table A1.02. The cost of phenol versus selectivity for various values of yield is shown in Fig. 1.06 for the air case, and in Fig. 1.07 for the oxygen case.

An estimated cost of £50/ton of phenol, which is close to its cost by the cumene oxidation process (Table 1.02), is assumed to be the criterion for the competitiveness of the vapour phase oxidation process.
Table L06

The economics of phenol production by the direct vapour phase oxidation of benzene for 1% phenol yield and 70% selectivity

(air as oxidant)

A. Cost of the process equipments:

(i) Recycle section:

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Cost £</th>
<th>% of total equipment cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>42,700</td>
<td></td>
</tr>
<tr>
<td>Heat exchanger and benzene vapouriser</td>
<td>75,000</td>
<td>69.2%</td>
</tr>
<tr>
<td>Cooler</td>
<td>7,500</td>
<td></td>
</tr>
<tr>
<td>Pumps &amp; Compressors</td>
<td>14,000</td>
<td></td>
</tr>
</tbody>
</table>

(ii) Phenol recovery system:

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Cost £</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Distillation columns with accessories)</td>
<td>62,000</td>
</tr>
</tbody>
</table>

Total equipment cost: 201,200

Capital (= 4 x equipment cost): 805,000

B. Phenol production cost

<table>
<thead>
<tr>
<th>Cost £/ton phenol</th>
<th>% of total cost of production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material cost</td>
<td>35.7</td>
</tr>
</tbody>
</table>

Cost accruing from recycle section

* Fixed charges (69.2% of total fixed charges) | 5.8 | 26.3 |

Utilities (80% of total utility cost): 8.6

Cost accruing from phenol recovery section

<table>
<thead>
<tr>
<th>Cost £</th>
<th>% of total cost of production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed charges (30.8% of total fixed charges)</td>
<td>2.5</td>
</tr>
<tr>
<td>Utilities (20% of total utility cost)</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Total: 54.8 | 100.0

By product credit: 1.6

Phenol cost: 53.2

* Fixed charges taken as 21% of capital.

(19 a)
N.B. The cost break down shows that the raw material cost (which depends on phenol selectivity) and the cost accruing from the recycle section (which depends on phenol yield) on the major cost factors. The yield and selectivity are mainly influenced by the reaction temperature, contact time and oxygen concentration in the feed and these variables together with the reactor inlet temperature were set as variables for the optimisation calculations.
Fig. 1.06

Cost of Phenol for Different Yields and Selectivities (Air Case)
Phenol Cost for Different Yields and Selectivities (Oxygen Case)
The value is 54% lower than the cost of phenol from toluene oxidation process on which commercial plants have been built. A straight line parallel to the axis at £50/ton (Figs 1.06 and 1.07) intercepts the corresponding yields for selectivities at which the process could be economically attractive. These yield-selectivity points plotted in Fig. 1.08 define the economically attractive regions of yield and selectivity. The area above Curve 1 is the economically attractive region for the oxygen case, while the area above Curve 2 is that for the air oxidation case.

The following observations can be made about the relationship:

1. A minimum selectivity around 45% is required at any yield for the cost to be below £50/ton. This is due to the high consumption of raw material at £25/ton at low selectivities being compensated by a by-product credit valued at fuel cost (£8/ton) for the present evaluation.

2. At lower yields the oxygen case requires lower selectivities than the air case and hence is more likely to be economically feasible.

At high yields (above 3.5%) the selectivities reported in the literature have always been below 35% which is far below the minimum required value of 45%. To get a yield of 8-9%, the process conditions required are such that degradation of phenol and a sharp drop in its selectivity occurs (Chapter 2). Hence it is unlikely that the process could be economically feasible at yields above 3.5-4%. This corresponds to a benzene conversion of about 8% taking 45% selectivity.

Extrapolation of the data for the promoter case of Lemetre and Caprara (38) by equation (ii) is shown by the dotted line in Fig. 1.08 and the difficulty in finding process conditions for an economic phenol
The Yield-Selectivity Relationships Defining the Economically Attractive Region

- Yield-selectivity relationship defining phenol cost of £50/ton (Oxygen Case)
- Yield-selectivity relationship defining phenol cost of £50/ton (Air Case)
- Yield-selectivity data of Lemetre & Caprara (38) with 1% ethanol as promoter
- Yield-selectivity data of Lemetre & Caprara (38) with pure benzene

Economically attractive region of yield & selectivity

Fig. 1.08

The Yield-Selectivity Relationships Defining the Economically Attractive Region
process by the direct vapour phase oxidation is clearly indicated. The economically optimum point lies between 1.5% yield (56% selectivity) and 1.0% yield (68% selectivity) where the cost of phenol could be very close to £50/ton. This corresponds to a benzene conversion range of 1.5-2.7% and production of .68-.94 ton phenol per ton benzene, considering 20% rise in yield of phenol on weight basis is due to increase in molecular weight. However, literature data on this range of conversion is very scarce.

1.6 Conclusions from the Process Evaluation Study and Comments

From the foregoing studies the conclusions made can be summarised as follows:

1. Most of the literature data for the direct vapour phase oxidation of benzene to phenol lies in the range of 4.0 to 10.0% phenol yield and it is unlikely that a process operating at this range could be economically attractive.

2. The use of oxygen instead of air as the oxidising medium would be marginally more economic.

3. There is very limited information on phenol yields below 4% but the limited information available indicates the possibility of improving the selectivity by lowering the conversion of benzene.

4. The use of a suitable promoter and investigations at low conversions might lead to economically more attractive results for a benzene oxidation process. An experimental investigation at low conversions might give us a better understanding of the kinetic mechanism of the process.
CHAPTER 2

Mechanism of Benzene Oxidation in the Gas Phase

and the Effect of Process Variables
CHAPTER 2

Mechanism of Benzene Oxidation in the Gas Phase and the Effect of Process Variables

The study of a process with valuable end products involves a search for the economically optimum condition for the reaction. The most reasonable method of finding this optimum condition is to search for it by elucidating the mechanism of the reaction, which can predict the course of the reaction over different ranges of the process variables.

Although hydrocarbon oxidation has been studied intensively for over fifty years, the oxidation mechanisms are still not very well understood because of the large number of free radicals and elementary reaction steps involved. Two quotations from recent reviews are relevant in this connection:

'It is as easy to derive a rate constant for a chemical reaction which does not occur as for one which does occur.' (40a)

'If there are more than two free radical intermediates, the mechanism cannot be deduced by kinetic study based upon analysis of all products and reactants.' (40b)

In this section the information available from the literature on benzene oxidation is discussed, with a view to understanding the mechanism of the process on the basis of currently established concepts of hydrocarbon oxidation. This may form the basis of developing rate equations and optimisation models in the subsequent chapters.

2.1 Current Views on the Mechanism of Hydrocarbon Oxidation (41)

It is generally agreed that hydrocarbon oxidations proceed through a free radical chain mechanism. Organic oxidations in the gas phase can
be divided into low temperature and high temperature regimes. There is a general agreement on what is termed a low temperature chain (up to 325-350°C):

\[ R^\cdot + O_2 \rightleftharpoons RO_2^\cdot \quad \text{(i)} \]

\[ RO_2^\cdot + RH \rightarrow R^\cdot + ROOH \quad \text{(ii)} \]

where \( R^\cdot \) is a hydrocarbon free radical.

Reaction (i) is exothermic (46 KCal/mole) and is predominant at low temperatures where competing reactions are absent. This chain mechanism predominates from 30 to 250°C producing hydroperoxides. Above 250°C the cool flame phenomenon occurs, and is characterised by induction periods and by the occurrence of pressure peaks. According to S. W. Benson (41) most of the present data seems to support the contention that cool flames arise due to the secondary decomposition of the hydroperoxides produced by the low temperature chains:

\[ ROOH \rightarrow RO^\cdot + \cdot OH \quad \text{(iii)} \]

Aldehydes also have been suggested as a facile source for secondary branching according to the reactions -

\[ RO_2^\cdot \rightarrow R'/CHO + \cdot OH \quad \text{(iv)} \]

\[ R'/CHO + ROO^\cdot \rightarrow RO + \cdot OH + RCO \quad \text{(v)} \]

\[ R'/CHO + O_2 \rightarrow RCO^\cdot + HO_2^\cdot \quad \text{(vi)} \]

The bond strength of hydroperoxide scission is about 43 KCal and frequency factors are around \( 10^{15} \) (42). With these parameters, the half life of a typical hydroperoxide could be around 1 second at 330°C. Such secondary initiations of radicals by peroxides or some other intermediates help to explain much of the oxidation phenomenology and have been termed 'degenerate branching' by Semenov (Fig. 2.01).
Between 325 and 450°C a region of negative temperature coefficient occurs in which the rate of oxidation decreases with the rise of temperature. This is ascribed to the failure of the system to produce alkyl hydroperoxide by reaction (i). Due to reversibility of reaction (i), the equilibrium concentration of alkyl peroxy radical decreases in favour of alkyl (R·) radical and high temperature mechanism predominates:

\[ R\cdot + O_2 \rightarrow R' = R'' + HO_2 \]  \hspace{1cm} (vii) \\
\[ HO_2 + RH \rightarrow H_2O_2 + R\cdot \] \hspace{1cm} (viii)

As a result, the relatively unstable alkyl peroxy radical is replaced by the more stable hydrogen peroxide. Now the secondary initiation (degenerate branching) responsible for cool flames is replaced by a much slower initiation - the second order decomposition of hydrogen peroxide -

\[ H_2O_2 + M \rightarrow 2 \cdot OH + M \] \hspace{1cm} (ix)

This reaction has an activation energy of 48KCal/mole and a lifetime of 1 second at 630°C. At 450-550°C it proceeds sufficiently rapidly to initiate the normal explosion limit in stoichiometric hydrogen-oxygen mixtures.
2.2 Chronological Review of Literature on Vapour Phase Benzene Oxidation

Since the unsuccessful attempt of Weiss and Downs (15) in 1920 to find any metal or metal oxide catalyst for direct synthesis of phenol from benzene, the homogeneous vapour phase oxidation of benzene has been the subject of a large volume of research work. The information available can be classified into two groups:

1. Investigations carried out under classical static methods to study the phenomenology of benzene oxidation, e.g. the ignition region, behaviour of the reaction at low and high temperature regions, and pressure-time relationship;

2. Investigations carried out under flow conditions with detailed product analysis and material balance at different process conditions.

Table 2.01 summarises the investigations on benzene oxidation reported in literature. The benzene structure is very stable to both chemical and thermal attack. The dissociation constant for benzene at 700°C is only 0.0034, i.e. about 0.3% of benzene is dissociated at this temperature (38).

A temperature range of 550°C to 680°C has been generally used for the study of benzene oxidation (Table 2.01). Most investigations have been carried out at atmospheric pressure in quartz reaction vessels.

2.2.1 Investigations Under Static Conditions

Phenol was first synthesised by homogeneous thermal oxidation by Mardles (43) in 1928. Studying auto-oxidation during slow combustion, he found that when 5% benzene vapour was added to a hexane-air mixture at 500°C, auto-oxidation of benzene occurred with phenol as one of the products.
### TABLE 2.01
Literature on Vapour Phase Oxidation of Benzene

<table>
<thead>
<tr>
<th>Reference</th>
<th>Static or Flow</th>
<th>Charge-stock</th>
<th>Promoters</th>
<th>Reactor</th>
<th>Temp. °C</th>
<th>Pressure</th>
<th>Contact time or LHSV</th>
<th>% Oxygen</th>
<th>Nature of investigation</th>
<th>Phenol Yield</th>
<th>Phenol Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>MARDLES, E. W. J. (43)</td>
<td>Flow</td>
<td>5% Benzene in hexane</td>
<td>-</td>
<td>heated quartz tube</td>
<td>520</td>
<td>1 atm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Traces</td>
<td>-</td>
</tr>
<tr>
<td>BIEB, C. H. (52)</td>
<td>Flow</td>
<td>-</td>
<td>HNO₃, NO-NO₂</td>
<td>1%</td>
<td>690-710</td>
<td>1 atm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FORT (47)</td>
<td>Static</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NEWITT &amp; BURGOYNE (51)</td>
<td>Static</td>
<td>Pure benzene</td>
<td>-</td>
<td>-</td>
<td>360</td>
<td>1 atm</td>
<td>-</td>
<td>4-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AMIEL (46)</td>
<td>Static</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BURGOYNE (44)</td>
<td>Static</td>
<td>Pure C₆H₆</td>
<td>dried and distilled</td>
<td>Silica 550 cc</td>
<td>480-560</td>
<td>P vs time</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BONE &amp; NEWITT (50)</td>
<td>Static</td>
<td>-</td>
<td>Steel</td>
<td>300-400</td>
<td>10-50 atm</td>
<td>-</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BURGOYNE, TANG and NEWITT (45)</td>
<td>Static</td>
<td>Pure benzene</td>
<td>-</td>
<td>Silica /Steel 570-640</td>
<td>1-15 atm</td>
<td>-</td>
<td>Stoichiometric</td>
<td>Ignition region</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>MOYER and KINGEL-HOEFER (53)</td>
<td>Flow</td>
<td>-</td>
<td>Pyrex glass</td>
<td>650</td>
<td>1 atm</td>
<td>-</td>
<td>-</td>
<td>(Patent)</td>
<td>49</td>
<td>48</td>
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<tr>
<td>Reference (Ref.)</td>
<td>Charge-Stock</td>
<td>Promoters</td>
<td>Reactor</td>
<td>Temp. °C</td>
<td>Pressure</td>
<td>Contact time or ( \text{LHSV} )</td>
<td>% Oxygen</td>
<td>Nature of investigation</td>
<td>Phenol Yield</td>
<td>Phenol selectivity</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>--------------</td>
<td>-----------</td>
<td>---------</td>
<td>----------</td>
<td>----------</td>
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<td>----------</td>
<td>------------------------</td>
<td>-------------</td>
<td>------------------</td>
<td></td>
</tr>
<tr>
<td>MOYER (54)</td>
<td>Flow</td>
<td>-</td>
<td>Quartz 3.7 mm</td>
<td>750-800</td>
<td>1</td>
<td>-</td>
<td>11</td>
<td>(Patent)</td>
<td>4.9-8</td>
<td>50-60</td>
<td></td>
</tr>
<tr>
<td>HARMAN (55)</td>
<td>Flow</td>
<td>Iodine 0.02%</td>
<td>-</td>
<td>600</td>
<td>1</td>
<td>-</td>
<td>11</td>
<td>Effect of iodine (Patent)</td>
<td>3-3.5</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>PORTER (56)</td>
<td>Discontinuous</td>
<td>-</td>
<td>Recovery furnaces</td>
<td>600-800</td>
<td>1</td>
<td>-</td>
<td>11</td>
<td>(Patent)</td>
<td>-</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>DENTON et al (57, 58, 59)</td>
<td>Flow</td>
<td>Pure benzene</td>
<td>Olefins, napthenes, ethers, alcohols 1%</td>
<td>Steel Coil</td>
<td>400-650</td>
<td>50-80</td>
<td>2-30 secs</td>
<td>Varied</td>
<td>Effect of promoters &amp; variables on phenol yield</td>
<td>4-5</td>
<td>30-35</td>
</tr>
<tr>
<td>IOFFE et al (60, 63)</td>
<td>Flow</td>
<td>Pure benzene</td>
<td>Tetralin ethylene oxide, alcohols 1%</td>
<td>Quartz</td>
<td>550-550</td>
<td>1</td>
<td>4-4.5 secs</td>
<td>7</td>
<td>Effect of promoters &amp; variables on phenol yield</td>
<td>2-7</td>
<td>17-35</td>
</tr>
<tr>
<td>DONALD et al (61, 70)</td>
<td>Flow</td>
<td>Benzene + 10% cyclohexane</td>
<td>-</td>
<td>Quartz ( \text{SN} = 1.67 )</td>
<td>550-600</td>
<td>1</td>
<td>1-2 sec</td>
<td>Varied</td>
<td>20-50</td>
<td>Phenol from impure commercial benzol</td>
<td>1-4</td>
</tr>
<tr>
<td>NORRISH &amp; TAYLOR (62)</td>
<td>Flow</td>
<td>Pure benzene</td>
<td>-</td>
<td>Quartz</td>
<td>685</td>
<td>1 atm</td>
<td>1 sec.</td>
<td>Varied</td>
<td>4-50</td>
<td>Product material, phenol yield</td>
<td>2-9</td>
</tr>
<tr>
<td>Reference</td>
<td>Static or Flow</td>
<td>Charge-stock</td>
<td>Promoters</td>
<td>Reactor</td>
<td>Temp. °C</td>
<td>Pressure</td>
<td>Contact time or LHSV</td>
<td>% Oxygen</td>
<td>Nature of investigation</td>
<td>Phenol Yield</td>
<td>Phenol Selectivity</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------</td>
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<td>-------------------</td>
</tr>
<tr>
<td>LEMETRE &amp; CAPRARA (38)</td>
<td>Flow</td>
<td>Analytical reagent-grade benzene</td>
<td>Me-OH, Et-OH, SeO₂, H₂S</td>
<td>Quartz</td>
<td>550-690</td>
<td>1 atm</td>
<td>1.25 secs</td>
<td>11</td>
<td>Product material bal., phenol yield</td>
<td>3-8</td>
<td>20-60</td>
</tr>
<tr>
<td>BEN-AIM &amp; DRILLAT (65)</td>
<td>Static</td>
<td>Pure benzene</td>
<td>-</td>
<td>Quartz</td>
<td>-</td>
<td>P vs time</td>
<td>-</td>
<td>-</td>
<td>Testing of kinetics on Semenov's model</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BEN DUNDEE (64)</td>
<td>Flow</td>
<td>Benzene</td>
<td>-</td>
<td>Fluidised sand</td>
<td>550</td>
<td>1-45</td>
<td>-</td>
<td>-</td>
<td>(Patent)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>URANO and HOSAKA (66)</td>
<td>Flow</td>
<td>Pure benzene</td>
<td>-</td>
<td>-</td>
<td>600-675</td>
<td>20 atm</td>
<td>-</td>
<td>2-5</td>
<td>Effect of oxygen on diphenyl synthesis</td>
<td>0.05-0.6</td>
<td>6-15</td>
</tr>
<tr>
<td>MIGITA et al (67)</td>
<td>Flow</td>
<td>Benzene</td>
<td>Cyclohexane, Br., I, SO₂Cl₂ Halogenated comp'd</td>
<td>Pyrex tube</td>
<td>600</td>
<td>1 atm</td>
<td>9 secs</td>
<td>11</td>
<td>Effect of promoters</td>
<td>0.4-5</td>
<td>-</td>
</tr>
<tr>
<td>EMPTE et al (68)</td>
<td>Flow</td>
<td>Benzene</td>
<td>Hydrogen 60-70%</td>
<td>Quartz packings</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7-10</td>
<td>Effect of hydrogen as promoter</td>
<td>-</td>
<td>60 higher</td>
</tr>
</tbody>
</table>
This was followed by a large number of investigations (1930-40) carried out with the classical method of noting the pressure-time relationship in a closed vessel (44-47). Discussions on some of their conclusions follow.

**Absence of Negative Temperature Coefficient**

Burgoyne (44) found that for benzene, the phenomenon of negative temperature coefficient was absent. Burgoyne, Tang and Newitt (45) had earlier concluded that the absence of a cool flame zone and negative temperature coefficient was due to the stability of the benzene molecule. Reactions of types (iii) and (vii) are absent with benzene at these temperatures.

**Products**

Very few of the authors working with the static system did detailed analyses of the stable products. Amiel (46) found small amounts of phenols but no peroxides. Burgoyne (44) found the products of oxidation to be mainly phenol and carbon dioxide. In addition, he reported the detection of formaldehyde, peroxides other than per-acids, ethylene, paraffin and traces of hydrogen - indicating rupture and cracking of benzene along with oxidation.

**Pressure-time Relationship and Reaction Kinetics**

Hinshelwood and Fort (47) found that the oxidation of benzene at 500°C was characterised by a long induction period. The reaction rate was found to vary greatly with hydrocarbon concentration, while the oxygen concentration did not have much effect. Pressure change versus time relationship was S-shaped with the maximum rate occurring at 50% conversion. Such a reaction is typical of a degenerately branched chain reaction. Earlier, Semenov (48, 49) had expressed the kinetics of degenerately branched reaction models with the expression

\[ r = \frac{1}{1 + e^{-\theta}} \]  

(\text{x})
When \( r \) is the fraction of reacted substance at a given moment of time, 
\( t' \) and \( \Theta = \Theta \times t_{\text{max}} \), \( t_{\text{max}} \) being the moment when the reaction rate reaches a maximum, and \( \Theta \) is a constant. Semenov (48, 49), using Hinshelwood and Fort's data, found that the benzene oxidation process can be described by the above equation.

Burgoyne (44) also showed that the reaction rate varied mainly with the concentration of the hydrocarbon but not with oxygen. For the oxidation at a temperature of 487°C, he found the order with respect to benzene to be 1.7 while with respect to oxygen it was 0.2. He also found that the reaction at low pressures was accelerated by nitrogen, possibly by slowing down the rate of breaking of the chain at the wall. Newitt and Burgoyne (51) found the reaction rate at high pressures to be decreased by nitrogen.

Amiel (46) in his studies with stoichiometric mixtures of benzene and oxygen found that the reaction rate expressed as percentage of benzene converted to CO and CO\(_2\) reached a maximum value almost at the beginning of the reaction and remained constant through the rest of the reaction. This contradicts Hinshelwood and Fort's (47) data, where the maximum rate is attained at 50% conversion. This is due to sensitivity of the chain reactions to various parameters, including effect of the vessel wall. Semenov (48) has proposed that displacement of maximum reaction velocity from 50% conversion to the origin of the scale can be caused by increased velocity of recombination of active centres (49). None of the above authors proposed any mechanism of benzene oxidation, except establishing it to be a degenerately branched reaction.

2.2.2 *Vapour Phase Oxidation Under Flow Conditions*

Several authors (63-78) investigated the oxidation under flow conditions. Most of the investigations were carried out in a quartz reactor at temperatures of 550-680°C and atmospheric pressure.
In some cases steel reactors and higher pressures were used.

Patents Survey

Between 1940 and 1950, a series of investigations followed under flow conditions, with a view to developing a commercial process for phenol production. This resulted in a number of patents (50, 53, 58). A typical example of such patented processes is a Solvay Process Co. patent which employs a temperature of 600-800°C, pressure of 0.5-2 atm and 2-45% oxygen in the feed. Another such process is from a Socony-Vac Co. patent which specifies a pressure in excess of 500 psi, a temperature of 350-500°C and the use of n-hexane as a promoter to the extent of 0.25-5.0% weight on feed.

Products - Yields and Selectivity of Phenol

Since 1950, reports on a number of investigations carried out with detailed product analyses, material balance and study of the effect of process variables were published in the literature. (38, 60, 68)

Phenol, diphenyl and oxides of carbon were found to be the main products in all cases. Norrish and Taylor (62) detected traces of catechol, hydroquinone, benzoquinone, terphenyls, maleic acid, fumaric acid and olefins. Little or no hydrogen has been detected in the products.

Yield of phenol from 0-10% at selectivities ranging from 0-60 mole% have been reported (Table 2.01). Some of the data (38, 60, 62) presented in Appendix II and plotted in Fig. 1.04, Chapter 1, for a preliminary evaluation of process economics shows that the selectivity increases as the yield is lowered. Organic promoters have been used to achieve higher yields and selectivities for phenol.

2.2.3 General Review

Bibb and Lucas (52) used nitric oxide and HNO₃ vapour as the oxidising agent and obtained 2% yield of phenol at 40% selectivity.
Harman (55), using air oxidation, found that iodine promotes the yield of phenol as well as its selectivity and obtained 47% selectivity at 3.0% conversion.

Norrish and Taylor (62) used pure benzene as the feedstock and at a reaction temperature of 685°C (1 atm) obtained 10% yield at 35% selectivity. All subsequent investigations were generally carried out in the presence of small quantities (0-10%) of organic promoters.

Denton, Doherty and Krieble (57-59), using a steel reactor and high pressure, found very little phenol in the products when pure benzene was used as the feedstock. Using cyclopentanes, olefins, ethers and isoparaffins (0.5-1% conc.) as promoters, they obtained improved yields and selectivities (3-5% yield, 20-30% selectivity). Comparing the data of Denton et al, the effect of promoters with pure benzene is presented in Table 2.02.

**TABLE 2.02**

<table>
<thead>
<tr>
<th>Pure Benzene</th>
<th>1b Phenol 100 lb C₆H₆</th>
<th>Phenol High Boilers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetratin</td>
<td>1.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Aniline</td>
<td>3.2</td>
<td>0.6</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>3.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Di-ethyl ether</td>
<td>3.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>3.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Donald Grover and Darlington (61, 70) studied the effect of various organic promoters and the effect of process variables on the oxidation of benzene - 10% cyclohexane mixture. Cyclohexane is an impurity in coal tar benzene and it is a good promoter for phenol as well.
I. I. Ioffe (69), Norrish and Taylor (62), Donald and Darlington (70) and Urano et al (66) have proposed mechanisms for the formation of products in the vapour phase oxidation. A controversy exists as to whether phenol is formed through phenoxy (C₆H₅O⋅) radicals or by the combination of phenyl (C₆H₅⋅) and hydroxyl (·OH) radicals.

W. Empte et al (68) studied the process using hydrogen along with oxygen. The presence of hydrogen is reported to have reduced some inconvenient by-products or completely eliminated them.

2.3 The Process Variables Affecting the Benzene Oxidation Reaction

Under Flow Conditions

The conversion of benzene and selectivity for phenol is known to be mainly affected by the following variables:

- Reactor material and design
- Homogeneous promoters and their concentrations
- Temperature
- Contact time
- Oxygen-benzene ratio
- Pressure
- Presence of inert gases in the system.

The effects of these variables are interdependent and, like most of the complex free radical reactions, benzene oxidation kinetics are very sensitive to small changes in the above variables. As a result, it is difficult to predict rates of product formation on the basis of postulated mechanism or semi-empirical relationships. Widely varying ranges of conversion and phenol selectivity are possible under different experimental set ups, although employing the same conditions of temperature, pressure, oxygen-benzene ratio and contact time (Table 2.01).

2.3.1 Reactor Material and Design

Quartz has been generally used as reactor material for benzene
oxidation because it is known to minimise the surface reactions. Denton, Doherty and Krieble (59), who used mild steel as reactor material under high pressures (60 psi), found that wt% yield of phenol increased from 2.0 to 4.5% and phenol/high boilers ratio improved from .2 to .85 on inserting a glass liner. Iron walls were found to promote complete combustion and condensation reactions. Nickel was found to be less active than iron.

Donald and Darlington (70), using quartz as reactor material, studied the effect of increasing surface to volume ratio from 1.67 to 6.0 on products. Carbon dioxide and water formation were found to rise with increase in surface to volume ratio, indicating that a quartz surface promotes combustion to some extent (Table A2.02, Appendix II).

A completely homogeneous free radical reaction is difficult to conceive except under high pressures.

2.3.2 The Effect of Promoters and Purity of Benzene

Most chain reactions are extremely susceptible to acceleration or retardation by traces of other substances, which may act by initiating desirable free radicals, terminating some radicals, or by participating in the propagation stage. Denton, Doherty and Krieble (59) found that the very impurities present in benzene act as promoters for phenol-forming reactions. Typical examples are cyclohexane and Me-cyclohexans. The organic promoters seem to be improving conversion to phenol by acting as homogeneous chain initiators, because of their greater instability compared with benzene. An analysis of the mechanism involved in promoter action is made in a later part of this section.

The promoters used by Denton, Doherty and Krieble (59) (cycloparaffins, olefins, ethers and isoparaffins) have been classified by them as follows:

1. Promoters which lower the 'optimum' reaction
temperature and increase the yield of phenol, e.g. cyclohexanol, cyclohexane, cyclohexanone, ethers etc.

2. Promoters which increase the phenol yield but do not affect the optimum temperature, e.g. aniline, carbon disulfide.

3. Promoters which lower the reaction temperature but have no effect on the yield of phenol, e.g. toluol, formaldehyde, etc.

Besides organic compounds mentioned above, chloroform, carbon tetrachloride (70), bromine (70, 73) and iodine (65) have been found to be effective promoters. Promoter concentrations of around 1% have been generally found to give maximum yield of phenol without any substantial loss in selectivity.

Donald and Darlington (70) investigated the nature of hydrocarbons acting as promoters. Using a number of diverse organic promoters such as chloroform, ether, amyl nitrate, they found that no particular grouping was essential for a good promoter. It was noticeable that compounds with weaker carbon-hydrogen bonds were the best promoters. The compounds were classified on the basis of the ease with which a hydrogen atom could be removed from it, and this criterion was expressed in terms of 'methyl radical attack value (MRA value)'.

\[ \text{MRA} = \frac{k'}{K} \]

where \( K \) and \( k' \) are the rate constants of the following reactions.

\[
\begin{align*}
\text{H-X + CH}_3 & \rightarrow \text{CH}_4 + X, \\
\text{C}_6\text{H}_5 - \text{H + CH}_3 & \rightarrow \text{C}_6\text{H}_5 + \text{CH}_4
\end{align*}
\]

(\( \text{where HX is the promoter} \))

Using promoters with different MRA values, they found that the improvement in yield of phenol was related to the increasing MRA values of the promoters (Fig. 2.02).
The above relationship is strictly between the nature of the promoter and yield of phenol or benzene feed per pass, and it does not say anything about selectivity for phenol. According to I. I. Ioffe et al (60,63), though the promoters used by them (propylene and cyclohexane) increased the benzene conversion and phenol yield per pass, the selectivity for phenol did not improve and sometimes decreased. However, data of Lemetre and Caprara (38) shows a definite improvement in selectivity as well as conversion through a range of temperatures, when ethanol is used as the promoter (Fig. 2.03). Denton et al (57, 59) also reported an improvement in the ratio of phenol to high boilers, or the use of promoters. They also noted that promoters which helped to lower the reaction temperature helped to improve the selectivity to a greater extent than the others.
2.3.3 The Effect of Temperature and Pressure

Phenol formation is reported mainly in the temperature range of 600-700°C (38, 70, 72, 73). Although normally no low temperature region benzene oxidation is noticed (57-59), using high pressure (1,500 psi), Denton et al (59) could obtain 1-2% yield of phenol at a temperature as low as 370°C. Donald and Darlington (70), using 10% cyclohexane as a promoter at atmospheric pressure, found a low temperature peak of phenol formation (350-400°C). However, tracer analysis showed that over 50% of the phenol produced came from cyclohexane (80%).

Fig. 2.03 presents some literature data on phenol yields and selectivities at various temperatures (vide Appendix II). Data of Lemetre and Caprara (38), who used very low concentrations of promoter (0.5-1%) of low MRA value (vide Fig. 2.02), shows sharp sensitivity of selectivity to temperature. The data on pure benzene (Curves 3, 4, Fig. 2.03) reported by Lemetre and Caprara is actually for analytical reagent grade benzene, which usually contains .3-.4% of impurities. The data of I. I. Ioffe et al and Donald and Darlington (Curves 5, 6, 7, 8), who used high concentrations of organic promoters (7-10%) and worked in a lower temperature range, shows that the selectivity for phenol is much less sensitive to changes in temperature. In all cases, selectivity increases down to 600°C temperature.

Denton et al (59) found that the promoters which lower the reaction temperature have the greater effect on improving both the selectivity and yield of phenol.

I. I. Ioffe (60) et al found that pure benzene could not be oxidised below 520°C. Phenol did not form until the temperature was 575°C. But thiophene-free coal tar benzene began to be oxidised with the formation of phenol at 490°C.

For higher conversions, the sensitivity of the reaction to the
(5) & (6) Donald and Darlington, 10% cyclohexane, 20-50% Oxygen, 2-3 sec. time

(1) & (2) Lometre & Caprara - Pure benzene 600-700°C; 50% Air; 1-1.5 sec. time

(3) & (4) - Do. - (.5 - 1.0 ethanol as promoter)

Fig. 2.03

Phenol Yield and Selectivity at Different Temperatures (Literature Data)
temperature could be extremely important due to high heat of reaction and the development of localised high temperature zones in the reaction tube. Denton et al (59), using an isothermal salt bath for temperature control, found that the conversion was extremely sensitive to even a 5°C change of temperature of the bath in cases where the reactor had relatively low heat transfer area.

Pressure has the effect of lowering the reaction temperature (59). Pressure is known to affect the rates of some propagation and termination reactions of free radicals, particularly peroxide decomposition. Data on the effect of pressure on benzene oxidation is scarce. Other possible effects of pressure are:

1. Decreasing wall effect, thus reducing cracking and combustion of benzene at the surface;
2. Higher benzene throughput per unit volume of reactor. In this case, temperature control could be poorer, there being more mass and hence more heat release per unit volume of the reactor.

2.3.4 Oxygen-Benzene Ratio

Norrish and Taylor (62), working with pure benzene at 685°C, found ignition to occur with a yellow flame as the oxygen-benzene ratio was raised to 1:1. All the curves for product yield versus \( \frac{O_2}{C_6H_6} \), except that for phenol, increased smoothly through the region of ignition. Phenol yield and selectivity register a sharp decline after ignition (Fig. 2.04), indicating its combustion when a certain oxygen-benzene ratio is exceeded.

For a given contact time, they found the selectivity to remain steady over a wide range as the ratio is made richer in benzene than 1:1 (Fig. 2.04, Curve 1).

Other oxidation products, including \( CO_2 \) yield, go up with increasing oxygen-benzene ratio. However, Norrish and Taylor (62) found oxygen
Fig. 2.04
The Effect of Oxygen-Benzene Ratio (Literature Data)
to inhibit diphenyl formation completely.

Donald and Darlington (70), who used 10% cyclohexane-benzene mixture as chargestock, found a similar relationship of yield and selectivity to oxygen-benzene ratio, but over a much narrower range of the variable (Fig. 2.04, Curves 2&2'). The greater sensitivity to oxygen-benzene ratio in their work could be due to the presence of cyclohexane, a more unstable component, at the conditions of benzene oxidation. Another point worth noting is that they found diphenyl yield also to increase with increase in oxygen-benzene ratio, unlike the results of Norrish and Taylor in this respect.

2.3.5 Contact Time

Generally, contact times of between .5 and 3 seconds have been employed in the investigations on benzene oxidation (60-63, 70). The only notable exceptions are Denton et al (59) who, using high pressure and lower temperatures, obtained a good yield of phenol at a contact time as high as 25 seconds.

Norrish and Taylor (62), who found ignition to occur above 1:1 O₂/C₆H₆ ratio, studied the effect of contact time at an O₂/C₆H₆ ratio at 5:6. Variation of contact time at this ratio did not lead to ignition under any condition. Yields of phenol, CO₂ and CO increased with the contact time until all the oxygen was consumed.

2.3.6 Other Variables

Denton et al (59) found that better premixing of benzene and air improved the phenol yield. Donald and Darlington found both yield and selectivity could be improved by addition of water vapour (5 moles per mole of benzene). Inert gases (68) were found to reduce combustion, possibly by reducing diffusion to the surface.
2.4 Mechanism of Benzene Oxidation in the Vapour Phase

Having gone through the available literature information, the possible free radical steps in the process are reviewed in this section. The postulated mechanism should be compatible with the established concepts of hydrocarbon oxidation (Section 2.1) and available information.

In spite of the large number of works on the oxidation of benzene, only a few authors have tried to put forward a reaction mechanism. No quantitative treatment of the data in support of any of these mechanisms is available in the literature.

I. I. Ioffe (69) found that the conversion of benzene is described by an S-shaped curve, while the kinetics are described by Semenov's (48) equation: eqn (x), Section 2.2.1. The above result, obtained under flow conditions, confirms the contention that the oxidation of benzene is a degenerately branched chain reaction.

I. I. Ioffe (69), Norrish and Taylor (62) and Urano et al (66) have proposed possible mechanisms of benzene oxidation. The activation energy of benzene oxidation has been found to be 56-64 KCal/mole by various authors. (44, 69)

2.4.1 The Initiation Reactions

The most obvious precursor to phenol and diphenyl - the main products - is the phenyl radical $\text{C}_6\text{H}_5^\cdot$. The phenyl radical has been detected mass spectrometrically in the pyrolysis of benzil by Ingold and Lossing (71).

In the case of pure benzene, the initiation could occur by thermal dissociation or by abstraction of a hydrogen atom by oxygen:

$$\text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5^\cdot + \text{H}^\cdot$$  \hspace{1cm} (xii)

$$\text{C}_6\text{H}_6 + \text{O}_2 \rightarrow \text{C}_6\text{H}_5^\cdot + \text{HO}_2^\cdot$$  \hspace{1cm} (xiii)
The bond strength of \( \text{C}_6\text{H}_5 - \text{H} \) has been determined to be 100 KCal/mole (72) and is equivalent to the activation energy for the reaction (xii). Reaction (xii) has been suggested by I. I. Ioffe as the initiation step. But in view of the high activation energy involved, Norrish and Taylor (62), and Urano et al (66) favour reaction (xiii) as the source of initiation. It is probable that the comparative ease with which some complex hydrocarbons are oxidised (particularly in the liquid stage) at 100–150°C is due to initiation processes of bimolecular nature such as:

\[
\text{RH} + \text{O}_2 \rightarrow \text{R}^* + \text{HO}_2
\]  

Quantum mechanical calculations have shown that a linear arrangement of the reacting molecules may cause this effect by lowering the actual potential barrier (48).

However, I. I. Ioffe et al (60, 63, 69) noted that the temperature of oxidation of pure benzene is higher than the temperatures at which pyrolysis of benzene takes place with sufficient velocity.

The amount of data on oxidation of pure benzene is very limited as most of the authors have used some promoters. Some of the data claimed by the authors (38) to be for pure benzene is not reliable, because even analytical reagent grade benzene contains 0.2–0.3% of impurities and it is difficult to remove traces of impurities like cyclohexane which has the same boiling point as benzene. Even a small amount of organic promoters are known to affect the benzene oxidation rate. The effect of the \( \text{MRA} \) value of the promoter on the reaction (fig. 2.02), and lowering of reaction temperature by the promoters strongly suggests that the promoters play a role in initiation reaction by their ability to decompose into free radicals. A promoter may produce free radicals either by a thermal dissociation or by reaction with oxygen.
\[ R_1R_2\text{-H} \rightarrow R_1^* + R_2^* \]  
\[ O_2 + R_1R_2\text{-H} \rightarrow R_1R_2^* + \text{HO}_2^* \]  
\[ R_1R_2^* + O_2 \rightarrow R_1R_2\text{OO}^* \rightarrow R_1R_2\text{OOH} \]

The free radical produced may then easily abstract a hydrogen atom from benzene, giving a phenyl radical:
\[ \text{C}_6\text{H}_6 + R_1^* \rightarrow \text{C}_6\text{H}_5^* + \text{RH} \]

2.4.2 Propagation Reactions and Formation of Phenol

After the formation of the phenyl radical, a number of possibilities may be considered for the propagation stage. The reaction may proceed through the action of \text{HO}_2 and hydroxyl radicals.
\[ \text{C}_6\text{H}_6 + \text{HO}_2 \rightarrow \text{C}_6\text{H}_5^* + \text{H}_2\text{O}_2 \]
\[ \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^* \]
\[ \text{C}_6\text{H}_5^* + \text{OH}^* + \text{M} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{M} \]

Alternatively, the reaction may proceed through peroxy radical formation:
\[ \text{C}_6\text{H}_5^* + O_2 \rightarrow \text{C}_6\text{H}_5\text{OO}^* \]
\[ \text{C}_6\text{H}_5\text{OO}^* + \text{C}_6\text{H}_5^* \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{O}^* \]
\[ \text{C}_6\text{H}_5\text{OO}^* + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{OOH} + \text{C}_6\text{H}_5^* \]
\[ \text{C}_6\text{H}_5\text{OOH} \rightarrow \text{C}_6\text{H}_5\text{O}^* + \text{OH}^* \]

In this connection, it is worth mentioning that the phenoxy radical (\text{C}_6\text{H}_5\text{O}^*) has been identified by Ingold and Lossing (71) in the pyrolysis of anisole.

Urano et al (66) has put forward the hydroxyl scheme (reactions xix-xxi). This is in keeping with the modern concept of oxidation reactions with more stable hydrogen peroxide playing a greater role at higher temperatures as branching agent (Section 2.1). In fact, in the case of propane oxidation (75), the reaction
\[ R^* + O_2 \rightarrow R' = R'' + \text{HO}_2^* \]  

47
has been shown to be 100 times faster than the reaction

\[ \text{R} + \text{O}_2 \rightarrow \text{ROO} \]  

at a temperature of 500°C.

However, certain objections could be made to the hydroxyl scheme -

1. In the case of pure benzene, reaction (xiii), i.e. abstraction of a hydrogen atom by oxygen, which is considered to be an unlikely reaction, has to play a major role in creating \( \text{HO}_2 \cdot \) radicals.

2. Substances like carbon tetrachloride \((\text{CCL}_4)\) and iodine \((\text{I}_2)\) are found to be good promoters for benzene oxidation and phenol formation. Since these substances have no hydrogen atoms, they are unlikely to contribute towards formation of \( \text{HO}_2 \cdot \) radicals.

3. Addition of hydroperoxides has not effectively promoted the oxidation reaction \((69)\).

4. Formation of phenol by reaction \((\times i)\) would result in the release of the \( \text{C}_6\text{H}_5-\text{OH} \) bond energy, which is in the order of 100 KCal/mole, and it would require a third body collision to stabilise the molecule. Phenol formation by such a three-body collision is unlikely.

An argument against the phenoxy \((\text{C}_6\text{H}_5\text{O})\) radical scheme is that no phenyl hydroperoxides \((\text{C}_6\text{H}_5\text{OOH})\) could be isolated by any of the authors working on the oxidation of benzene. However, unlike alkane oxidation reactions, the phenoxy radical need not be generated by the fission of the hydroperoxide.

I. I. Ioffe \((69)\) has proposed the formation of phenol by the reaction of phenoxy and phenyl peroxy \((\text{C}_6\text{H}_5\text{OO} \cdot)\) radicals according to
the schemes shown in reactions (xxii-xxiv).

Reaction (xiii) requires redistribution of the oxygen bond which, according to I. I. Ioffe (69), is fully possible for a complex aromatic molecule, although analogous conversion for simple molecules is considered less probable. The activation energy required for such a redistribution would not be an inhibiting factor at the high temperatures in which benzene oxidation takes place.

2.4.3 Formation of Carbon Dioxide

The high yield of phenol generally obtained shows that it is quite a stable compound at the temperature of investigation. The presence of a hydroxy group is likely to facilitate further hydroxylation in ortho- and para-positions. Pyrocatechol and quinol have in fact been found by Norrish and Taylor (62) in the reaction product. According to them, the oxidation of phenol to a dihydroxy derivative proceeds by the same scheme as the oxidation of benzene to phenol, put forward by them:

\[
\begin{align*}
C_6H_5OH + O_2 & \rightarrow C_6H_4OH + HO_2 \quad (xxvii) \\
C_6H_4(OH) + O_2 & \rightarrow C_6H_4(OH)OO- \quad (xxviii) \\
C_6H_4(OH)OO- + C_6H_6 & \rightarrow C_6H_4(OH)_2 + C_6H_5O^- \quad (xxix)
\end{align*}
\]

The dihydroxy derivative formed then undergoes oxidation which leads to decomposition:

\[
\begin{align*}
\text{[Picture of chemical structures]} \quad (xxx)
\end{align*}
\]

\[
\begin{align*}
\text{[Picture of chemical structures]} \quad (xxxi)
\end{align*}
\]
Actually, maleic acid and acetylene were found in the products by the above authors.

I. I. Ioffe has proposed a slightly different route to carbon dioxide formation - through formation of poly-oxy compounds, according to the reactions:

\[
\begin{align*}
\text{OH}^+ + \text{R} \rightarrow \text{OH}^- + \text{RH} & \quad (\text{xxxvii}) \\
\text{OH}^- + \text{O} \rightarrow \text{OH-O} + \text{H}^+ & \quad (\text{xxxviii}) \\
\text{OH-O} + \text{R} \rightarrow \text{OH}^- + \text{RH} & \quad (\text{xxxix})
\end{align*}
\]

and so on, until the formation of either single or multi-nuclear poly-oxy compounds. Some of these compounds easily undergo complete decomposition of the nucleus with separation of oxides of carbon and complete oxidation of the fragments takes place.

2.4.4 Formation of Diphenyl

Diphenyl could form by two possible reactions:

\[
\begin{align*}
\text{C}_6\text{H}_5^- + \text{C}_6\text{H}_6 & \rightarrow \text{C}_{12}\text{H}_{10} + \text{H}^- & \quad (\text{xxxv}) \\
\text{C}_6\text{H}_5^- + \text{C}_6\text{H}_5^- & \rightarrow \text{C}_{12}\text{H}_{10} & \quad (\text{xxxvi})
\end{align*}
\]

To find out which of these two reactions is responsible for diphenyl formation, Norrish and Taylor carried out pyrolysis of benzil - which easily gives phenyl radicals - in the presence of benzene. Diphenyl produced was roughly equivalent to the moles of benzil decomposed, and hydrogen was not found in the products. These results confirm occurrence of reaction (xxxvi). If reaction (xxxv) had been responsible for diphenyl formation, yield of diphenyl was likely to have been greater than the quantity of benzil decomposed.

2.4.5 The Role of Reactor Surface

The wall effect is a very common phenomenon in free radical reactions and the course of oxidation reactions can be profoundly affected by the surface of the reactor.
All surfaces commonly used in process studies are known to decompose peroxide. Satterfield and Reid (73), studying propane oxidation in a boro-silicate reactor, found that hydrogen peroxide isolated in the products was less than 50% of the quantity expected from the reactions:

\[
\begin{align*}
C_3H_7^{-} + O_2 & \rightarrow C_3H_6 + HO_2^{-} \\
C_3H_8 + HO_2 & \rightarrow C_3H_7^{-} + H_2O_2
\end{align*}
\] (xxxvii) (xxxviii)

Theoretical calculations from established data indicated only 2-10% of the hydrogen peroxide formed could decompose in the homogeneous reaction. Surface effects increase with temperature. At temperatures over 600°C, most of the hydrogen peroxide is likely to decompose in the vessel wall by the reaction:

\[
H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2
\] (xxxix)

This reaction reduces the role of the hydroxyl radicals in phenol formation in the vapour phase.

Reactor surface is also known to promote cracking reactions. Satterfield and Reid (73) established in their study on propane oxidation that most of the ethylene formed was due to the reaction of propyl radicals at the wall -

\[
C_3H_7^{-} \text{wall} \rightarrow C_2H_4 + CH_3^{-}
\] (xl)

They found a highly combustible brown film on the vessel wall attributable to polymerisation of the olefins.

Rice and Herzfield (74) have observed that pyrogenic decomposition studies gave abnormal results in clean glass and boro-silicate surfaces, and that reproducible results are obtained only when the surface is conditioned by being covered with a carbonaceous film. However, in oxidation studies, continuous removal of the film by combustion is likely to occur. Dardin and Albright (75) noted the existence of such a carbonaceous film on the reactor surface in their study on propane oxidation. The reactor surface was found to be activated after a certain
time of operation, resulting in a lower temperature requirement for the same conversion. They attributed these phenomena to the formation of the carbonaceous film which reached equilibrium after running for some hours.

Oxidation of benzene takes place at a much higher temperature than propane oxidation. At such temperatures, both action of the surface due to its polarity, in producing carbonaceous products, and subsequent combustion of these to oxides of carbon, have tremendous roles to play.

Phenol is quite a stable compound, like benzene, and it is likely that most of the carbon dioxide and monoxide comes from surface reaction at low conversions.

The effect of surface volume ratio investigated by Donald and Darlington (70) is noteworthy (sec-2.3) in this connection.
CHAPTER 3

Discussion and Scope of the Present Work
CHAPTER 3

Discussion and Scope of the Present Work

3.1 Discussion

In the first chapter it was shown that the benzene oxidation route to phenol could be economically competitive with the existing commercial processes at any benzene conversions above 7% provided that high selectivities (56-100%) for phenol could be obtained. Unfortunately, experimental data at such low conversions of benzene is scarce in the literature and an experimental investigation in this range of conversion is necessary.

The literature data also shows that it might be possible to obtain such values of conversion and selectivity by the use of a promoter. 0.5 to 1% concentration of promoters appears to be effective for enhancing the production of phenol. Compounds acting as promoters are relatively unstable compared with benzene at the temperatures of benzene oxidation (section 2.3), and are likely to decompose to give many by-products. Hence, a high concentration of promoter would be undesirable.

Any process using a promoter that decomposes during the reaction would require make-up supply of the promoter. Information in the literature about the rate of promoter consumption is scarce because most of the data is confined to the conversion of benzene and oxygen feedstocks only. A study on the rate of the promoter conversion and the products formed from the promoter should also throw light on the mechanism of promoter action.

The mechanism of carbon monoxide and carbon dioxide formation is not suitably explained by the available literature (sections 2.4.3 and 2.4.5). The existing theories interpret the formation of oxides of carbon through the decomposition of phenol by formation of poly-phenyls (69) or through dihydroxylation of phenol and subsequent rupture of the ring (62). Existing data supports the concept of further oxidation of phenol at high conversions and where a high oxygen-benzene ratio is used (Fig. 2.04). But in low conversion ranges and with low oxygen
concentration in feed, decomposition of phenol might be avoided and a
different mechanism of combustion might occur.

The kinetic analysis from the pressure versus time data (section
2.2.) shows the order of the reaction to be over 1 with respect to
benzene, and near zero with respect to oxygen. The pressure-time
relationship in the studies mentioned in section 2.2. were influenced
mainly by carbon monoxide and carbon dioxide formation. At high
selectivities for phenol the order of the reaction could be very
different.

Due to the influence of the surface in free radical reactions and
under different ranges of process conditions, a wide variety of mecha­
nism of benzene oxidation is possible, with certain reactions dominating
at particular experimental conditions. The aim of the project is:
1. To obtain an understanding of the mechanism of benzene oxidation
at low conversions (0-4.0%) with or without the use of a promoter.
2. To develop a reaction rate model applicable to low conversion
conditions so as to predict the product yields over a range of
operating conditions.
3. Use of the reaction rate model for process optimisation in order
to find the optimum process conditions. The optimum process
condition in this context means the process conditions at which
the cost of phenol production by the process would be minimum.

3.2 Experimental Investigations Planned

The experiments planned for the present study were:
1. Air oxidation of pure benzene:
The effects of the following variables were to be studied.
   Contact time       .5 to 3.0 seconds
   Temperature        370-650°C
   Oxygen concentration .5 to 10% in feed
   Pressure           1 atm
2. The oxidation of benzene - promoter mixture with air:

The effect of variables in the operating range mentioned for pure benzene were to be investigated with feedstock containing .5-1% of a promoter with benzene.

Comparison of the results of oxidation with a promoter with that for the pure benzene oxidation could give a better understanding of the role of the promoter.

3. Pyrolysis of benzene:

Pyrolysis of pure benzene and benzene containing a promoter at the temperature range used for the oxidation reactions would reveal the following:

(1) the ability of pure benzene to initiate phenyl radicals in the absence of oxygen,
(2) the extent of promoter effect in the initiation of the phenyl radical formation.

3.3. Choice of the Promoter

The effects of a wide variety of promoters on phenol yields have been studied by several authors (section 2.3). However, in all the investigations, emphasis has been given to the effect of the promoter on phenol yield and little has been said about the selectivity for phenol.

High yields of phenol are obtained by the use of promoters having high 'methyl radical attack' rate, as established by Donald and Darlington (Fig. 2.02, section 2.3).

Using a promoter of high MRA value, it should be possible to improve phenol selectivity by lowering the conversion with changes in variables like temperature, oxygen concentration and contact time.

The choice of the promoter was made on the following criteria:

1. The promoter should have a high MRA value (vide Fig. 2.02).
2. From a practical point of view, it should be possible to identify and measure the promoter and its decomposition products by simple methods.

3. Compounds like cyclohexane, methyl cyclohexane or cyclohexanone should be avoided because Donald found (70b) that in benzene oxidation studies he made with cyclohexane as a promoter, some of the phenol formed was from cyclohexane. Chloroform was chosen for the present investigations since it satisfied most of the desirable criteria.
CHAPTER 4

The Description of Apparatus and Experimental Techniques
CHAPTER 4
The Description of Apparatus and Experimental Techniques

The apparatus was designed to function as a single pass flow system in the following range of operating conditions:

- Temperature - up to 700°C
- Pressure - 0-100 psig
- Contact time - 0-3 seconds
- % Oxygen in feed - .5-50

Because of the design temperatures and pressures, steel was used as the material of construction for the whole apparatus. The reactor and the connecting tubes subject to high temperatures were of type 316 stainless steel. However, due to intensive surface reactions with the stainless steel reactor (vide Chapter 6), it had to be lined with quartz as described in the following sections.

4.1 Flow Description of the Apparatus

A sketch of the experimental apparatus is given in Fig. 4.01. Benzene from the receiver is pumped by a calibrated micro-pump (0-30 cc/min) into the vaporising and preheating furnace. Air is drawn from the main supply (100 psi) through a pressure reducing valve and a calibrated rotameter (0-1,400 cc/min) into the preheater. The preheater is set at the reaction temperature and sufficient tube length is allowed for the reactants to be heated close to this temperature. The two streams are then mixed and passed into a quartz-lined tubular reactor kept in a furnace at the reaction temperature. The reactor effluents are immediately quenched in a series of two water coolers. The condensed liquid is separated in a drum separator from where it is removed for analysis. Normally, the amount of liquid sample per run was about 200 cc. A needle valve at the separator outlet controls the pressures. The gases are passed through a cold trap, packed with ice-salt mixture, and then through an absorbing vessel before being vented. Gas samples are withdrawn from
The Experimental Set Up
time to time for orsat analysis.

4.2 The Reactor

The reactor consists of a 22-inch long and \( \frac{\delta}{4} \)-inch diameter type 316 stainless steel tube lined with a close fitting quartz tube of the same length. The annular space between the metal and quartz tubes was packed with glass wool to minimise the flow of the reactants through the space. Fig. 4.02 presents a sketch of the reactor tube together with fittings.

The bare tube from the benzene-air intersection to the reactor was also lined with a quartz tube. The volume of this tube (2.5 cc) was very small compared to reactor volume (74 cc).

![Fig. 4.02](image)

The mixing of the air and benzene vapour before the reactor was assumed to be complete due to (1) opposing direction of the two streams in the T joint and (2) change in size and direction at the joint (Fig. 4.02). The mixing section was heavily insulated.

4.3 Temperature Measurement and Control in the Reactor Furnace

The reactor is placed in a block furnace of the dimension (24" x 8" x 16"), with the heating coil wound around a 3-inch diameter bore along its length (Fig. 4.03). A sharp temperature gradient was found to exist along the reactor length, due to heat losses from the two ends of the bore, despite closer winding of the coil towards both ends. The radial temperature gradient, along the bore diameter, was also high.
Temperature profile after metal rod packing and insulation

Temperature profile without packing and insulation

Fig. 4.03

Fig. 4.04

Temperature Profile Along Furnace Bore Length
In order to obtain a uniform temperature throughout the bore, the following steps were taken:

1. The space around the reactor was packed with steel rods of the same length as that of the reactor.
2. Both ends of the furnace bore were insulated with asbestos packing.

The resulting temperature profile is shown in Fig. 4.04. The temperature gradient between the reactor wall and the furnace bore wall was found to be negligible.

Two thermocouple slots were provided, one along the reactor wall, and another in the annular space between the furnace bore and the reactor. The reactor wall temperature was assumed to be the reaction temperature. The furnace had an on-off temperature control. The temperature change of the gases due to heat of reaction was assumed to be negligible at low conversions of benzene.

The preheater is a block furnace with two 1-inch bores (3' long), with an on-off temperature control.

For each run, temperatures were noted at the reactor wall (at different points) and the preheater outlet (bore).

The calibration of the pyrometer is given in Appendix 3 (Fig. A3.01).

4.4. Flow Measurement

The air flow was measured with a rotameter at the inlet of the system and the flow of reactor effluent gases was measured by a bubble flow meter. The calibration of the rotameter is given in Appendix 3 (Fig. A3.02). The rotameter was calibrated with respect to a standard bubble flow meter.

The benzene flow was roughly set with the calibrated micro-pump (Appendix 3, Fig. A3.03). Accurate measurement of the flow was then made with the graduated level gauge. On closing valves V1 and V2 (Fig. 4.01), the pump draws liquid from the level glass only and the rate of change of
level with time gives the flow rate (Appendix 3, Fig. A3.04).

4.5 Analytical Procedure

Gases: The gases were analysed in a standing orsat apparatus. The analysis was made for CO$_2$ (using KOH solution), O$_2$ (alkaline pyrogallol solution), CO (ammoniacal cuprous chloride solution) and olefinic gases (bromine water). Pyrogallol and cuprous chloride solutions, which are very quickly exhausted, were prepared freshly for each set of runs.

When chloroform was used as a promoter, the gases were passed through standard .2N silver nitrate solution kept in an absorber. The silver nitrate solution from the absorber was titrated with standard sodium chloride solution in order to find the quantity of hydrogen chloride absorbed.

Liquid Sample: A part of the liquid sample from the separator drum was analysed in a chromatograph, without any further treatment. A Perkin-Elmer series 800 chromatograph was used with the following operating conditions for phenol and diphenyl:

- **Column**: Apiezon 'L'
- **Sample size**: Microlitres
- **Nitrogen flow**: 30 cc/min
- **Detector**: Hydrogen flame ionisation
- **Injector block temperature**: 300°C
- **Column temperature**: 130°C for 5 minutes
  - Programmed 130-250°C @ 20°C/min
  - (6 minutes)
  - Steady at 250°C for 13 minutes
- **Total time**: 24 minutes

P-cresol was used as a marker and the relative height of the peaks with respect to that of the marker was taken as the basis of calibration. (Appendix 3, Fig. A3.05)
Chromatogram of Reaction Products

Fig. 4.05
The water content in the feed as well as liquid products was analysed by a Fischer apparatus (76) to determine the quantity of water formed by the combustion reactions.

The bulk of the liquid sample was then fractionally distilled, using a packed column (eqv. 5 theoretical plates) with a reflux ratio of about 3 or 4:1. The first 10% and the last 10% samples were collected for analysis, the remainder being pure benzene. A cold trap similar to the one used in the apparatus (Section 4.1) was used with the distillation set up.

For the lighter samples (i.e. the first 10% of the distillate, the condensate of the cold trap or the benzene feedstock), the chromatographic analyses were made under the following conditions:

- Column: Di-isn-decyl phthalate
- Nitrogen flow: 30 cc/min
- Detector: Flame ionisation
- Column temperature: 80°C

As only traces of cracked products were found in the lighter fractions of the sample, no calibration was required. Typical sample chromatograms for the reactor effluent liquid are given in Fig. 4.05.

The cold trap condensates and the light distillate samples from runs with chloroform as promoter, contained some residual promoter. The amount of promoter could be determined with reasonable accuracy ±5% with calibration, using relative peak heights of benzene and chloroform.

A typical chromatogram of cold trap condensate is presented in Fig. 4.06.

4.6 Preparation of the Chargestock

As reproducibility of the results depended on consistency of chargestock purity (Chapter 6), Analytical Reagent grade benzene (.3 to .5% impurities) was further purified in a fractionating column under
Fig. 4.06  
Chromatogram for Light Distillate

Fig. 4.07  
Chromatogram for Analytical Reagent Grade Benzene

Fig. 4.08  
Chromatogram for Pure Benzene
the following operating conditions:

Theoretical plates - 15
Reflux ratio - 10:1.

The first 10% and the last 10% of the distillate were rejected and the remainder of the stock was regarded as 'pure benzene'. The chromatograms of the Analytical Reagent Grade benzene and pure benzene are presented in Figs 4.07 and 4.08 respectively. The impurities in the benzene were identified by the usual chromatographic technique.

4.7 Experimental Techniques

The benzene receiver was first filled with impure benzene stock for recirculation during the start up period. The benzene and air circulation were adjusted to the desired rates as the two furnaces were switched on at full load. When the desired temperatures were reached, the temperature controllers were set to the desired levels. The system was allowed to stabilise at the reaction temperature for 1-1½ hours and the gases were analysed from time to time to check if the analysis remained constant. Then the receiver stock was replaced with pure benzene with and without known quantity of promoter.

After 15-20 minutes, the separator drum was drained out, the gases were channelled through the cold trap and the run was started. The duration of a run was from 25 to 50 minutes during which the gases were analysed by orsat apparatus. The liquid samples from the separator drum and cold trap were collected for analysis at the end of the run.

After every 15-20 runs, one of the earlier runs was repeated in order to find out whether reproducibility was affected by ageing of the reactor. No such effect was noted.

The contact time was varied by varying the flow rates of the components. The oxygen content in the feed and constant contact time was varied by simultaneously adjusting both benzene and air flow rates so as to keep the total molal flow rate of the feed constant.
The oxygen content in feed was usually from 0.5 to 7% (14 fold). Corresponding change in the concentration of air was from 2.4 to 33.0% in feed. To maintain a constant flow rate of the feed (for a constant contact time), the benzene flow rate had to be adjusted, resulting in variation in its concentration in the feed from 97.6% to 67%. The change in benzene concentration is very small over the range in which oxygen concentration is varied 14 fold and hence the experimental results would reflect only the effect of varying oxygen concentration.

It is assumed that the nitrogen in the feed has no effect on the reaction.

4.8 Method of Calculation and Typical Experimental Result

It is difficult to establish an absolute material balance for benzene at low conversions unless a recycle system is used. Thorough analyses of the liquid samples were made chromatographically and the gas was analysed for olefins and oxides of carbon.

The conversion of benzene was calculated on the basis of 100% carbon balance with the products identified and measured quantitatively (phenol, diphenyl, CO and CO₂). For the interpretation of the experimental data, the definitions of conversion and selectivity were modified as follows:

\[
\text{conversion} = \frac{\text{Moles of benzene converted to CO, CO}_2, \text{phenol and diphenyl/HR} \times 100}{\text{Moles of benzene passing through the reactor/HR}}
\]

\[
\text{selectivity} = \frac{\text{Moles of benzene converted to phenol} \times 100}{\text{Moles of benzene converted to phenol, diphenyl, CO, CO}_2}
\]

Oxygen balance was checked by comparing the amount of unreacted oxygen from orsat analysis of the gases with the value obtained by subtracting the total amount of oxygen contained in the phenol, CO, CO₂ and water from the amount of oxygen in feed. The two values agreed within an error of ±3%.

* Vide other definitions in page 160.
Table - 4.01

Conversion calculations (pure benzene)

Run 114 (Appendix - 4)

Reaction conditions: Temperature = 670° C, Contact time = .78 sec., Oxygen conc. = 5.5 mole% in feed
(Air = 26% and Benzene 74% in feed).

Basis: 100 moles of benzene,
7.45 moles of oxygen as input.

Products:
- Phenol = .563 mole
- Carbon dioxide = 3.08 moles
- Diphenyl = .396 mole
- Carbon monoxide = .34 mole
- Water = 1.55 moles

1 mole of benzene (C6H6) gives 6 moles of Carbon oxides and 2 moles of benzene combine to give 1 mole of diphenyl.

Benzen conversion = \[
\frac{.563 \times 2 \times .396 + 3.08 + .34}{6} = 1.92 \%
\]

Phenol selectivity = \[
\frac{.563}{1.92} \times 100 = 29.4 \%
\]

Computed consumption of oxygen =
\[
\frac{.5 \times .563 + 3.08 + .5 \times .34 + .5 \times 1.55}{4.31} = 4.31 \text{ moles}
\]

Estimated oxygen conversion = \[
\frac{4.31}{7.45} \times 100 = 57.8 \%
\]

Actual oxygen conversion (Orsat Analysis) = 58.0 %

Table - 4.02

Conversion calculations (promoter case)

Run 214 (Appendix - 4)

Reaction conditions: 610° C, 5.5% oxygen in feed, .75 sec. contact time.

Basis: 100 moles of benzene,
7.45 moles of oxygen and .65 mole chloroform as input.

Benzene and oxygen conversion calculations similar to that shown in Table - 4.01.

Chloroform output in product stream = .47 mole.
Chloroform consumption = .55 - .47 = .08 mole.
HCl in product stream = .39 mole

A complete conversion of chlorine atoms in Chloroform to HCl would give 3 moles of HCl per mole of Chloroform consumed.

""" Chlorine balance obtained = \[
\frac{.39}{.18} \times 3 \times 100 = 72 \%
\]

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When chloroform was used as a promoter, the chloroform conversion was estimated separately by measuring the chloroform content in the feed and the product streams. It was found that \(60\%\) by weight of the chloroform converted was accounted for by hydrochloric acid absorbed from the outgoing gas stream by standard silver nitrate solution. As the chlorine content of chloroform is about \(90\%\) by weight, the chlorine balance was not complete and some of it remained unaccounted for. A part of the chloroform converted could have contributed to the formation of oxides of carbon. However, only a small part of the total carbon oxides formed could have come from the chloroform. The whole of the combustion reaction was attributed to benzene (Table 4.02) as per the previous definition of benzene conversion.

Sample calculations from experimental observations are presented with pure benzene and benzene containing chloroform as promoter in Tables 4.01 and 4.02 respectively.

**Experimental Errors**

The following are the range of errors in the measurements and product analysis:

- Orsat analysis - Oxygen \(\pm 2\%\); \(CO_2\) \(\pm 1\%\); \(CO\) \(\pm 5\%\)
- Phenol yield \(\pm 1\%\) at yields over \(.2\%\)
- Diphenyl yield \(\pm 5\%\) at yields below \(.2\%\)
- Temperature \(-\pm 2^\circ C\)
- Flow rate \(-\pm 2\%\)

**4.9 Discussion on Methods Used by Other Investigators**

Most of the previous investigators used chemical methods of analysis. Denton et al (59), Norrish and Taylor (62) and Donald and Darlington (80) measured phenol yield by a caustic extraction and bromination method. Denton et al separated heavy residue from benzene by fractionation, subtracted the amount of phenol from it and termed the remainder as 'high boilers'.
Norrish and Taylor (62) used an extensive analytical technique using chemical methods for detection of maleic acid, formic acid, formaldehyde, catechol, quinol and other phenolic compounds, and hydrogen. However, only traces of these could be detected.

Donald and Darlington (70) carried out ultraviolet analysis of the product and established that the high boiling components were mainly phenol and diphenyl, and that no other heavy compounds were present. They established benzene % in products by refractive index, and the rest as % residue. Then phenol was determined by bromide-bromate method and the remainder of the residue was assumed to be diphenyl.

The gases were passed through cold traps and analysed by Orsat apparatus in all cases.
CHAPTER 5

The Experimental Results
CHAPTER 5

The Experimental Results

5.1 Experimental Investigation

The experimental work falls into three broad groups:

Set 1: Experiments with pure benzene and air; effects of traces of impurities in the benzene feedstock.

Set 2: Oxidation of benzene with air in the presence of a promoter (chloroform).

Set 3: Experiments on the pyrolysis of pure benzene and of benzene containing a promoter (chloroform).

The experiments were carried out in a quartz lined reactor. The effects of contact time, feed composition (benzene, air and promoter) and temperature were studied at atmospheric pressure. The operating conditions were adjusted to obtain a benzene conversion range of 0.1 to 3.5% and oxygen conversion up to 60-70%. The range of operating conditions in sets 1 to 3 were:

- Contact time - 0.4-1.4 seconds
- % Oxygen in feed - 0.0-10.0%
- Promoter - 0-1% weight on benzene

The experimental results are tabulated in Appendix 4.

As stated earlier (Chapter 4), a set of runs (set 0, Appendix 4) were carried out with a stainless steel reactor in the temperature range of 350-600°C. The products consisted of carbon dioxide and traces of diphenyl but no phenol could be obtained under any conditions, with or without a promoter. The severe combustion attributed to reactor surface catalysis, was eliminated by lining the reactor with a quartz tube.

Experiments were carried out with the stainless steel reactor and the quartz lined reactor to compare the results. In each case, the
Comparison of Product Yields for Stainless Steel and Quartz Reactors

(0.6 sec., 2.4% Oxygen)
experimental runs were carried out at different temperatures but at the same conditions of contact time, concentration of oxygen in the feed, and with the same benzene feedstock. At each temperature, the system was allowed to stabilise for \( \frac{1}{2} - 2 \) hours before the start of a run.

The experiments were carried out in the following temperature sequence.

<table>
<thead>
<tr>
<th>Steel Reactor</th>
<th>350 375 400 455 480 510</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C)</td>
<td>530 570 530 505 450 400</td>
</tr>
<tr>
<td>Quartz Reactor</td>
<td>350 400 450 500 550 605</td>
</tr>
<tr>
<td>(°C)</td>
<td>625 645 620 605 550</td>
</tr>
</tbody>
</table>

Thus, after the completion of the run at the maximum temperature in each case, the runs at lower temperatures were repeated. The results, plotted in Fig. 5.01, have the following points worth noting:

1. In the stainless steel reactor combustion takes place at a temperature as low as 375°C, whereas in that with the quartz liner, no trace of oxidation or pyrolysis was found below 500°C.

2. With the stainless steel reactor, the carbon dioxide yield follows: Curve 1 when the incremental temperature changes are upward along the temperature scale, and Curve 2 when the incremental temperature changes are downwards. The hysteresis Curve 1-2 was found to be reproducible within \( \pm 5\% \). At higher temperatures, the surface undergoes a temporary change, possibly by deposition of carbonaceous material (vide Section 2) and the resulting combustion consumes all the oxygen (Fig. 5.01). No such effect was noticeable with the quartz lined reactor.

3. Since no carbon dioxide was detected below 500°C after the quartz liner was put in, it can be concluded that only a negligible portion of the feed mixture passes through the annular space between the quartz liner and the outer
Henceforth, all the discussions will relate to the experiments with the quartz reactor only.

5.2 Preliminary Observations on the Experimental Results: Pure Benzene Case

Having established arguments for and against different mechanisms of product formation (Chapter 2), it is now necessary to look into the effects of variables shown by the present experimental data, in order to develop a simple mechanistic model for the oxidation of pure benzene.

5.2.1 Products

The main products in all cases were phenol, diphenyl, carbon dioxide, carbon monoxide and water.

Small amounts (in the order of 2 - 3% of benzene converted) of other products such as maleic acid, diphenyl oxide, catechol and naphthalene were observed. A typical chromatogram of an experimental sample containing the products is shown in Fig. 4.05 (Chapter 4).

5.2.2 The Effect of Benzene Purity

Runs with different stocks of Analytical Reagent Grade benzene gave different results under similar operating conditions and the reason was found to be the varying amounts of impurities (.3 - .5%) in the different benzene stocks.

A uniform benzene stock was obtained by purifying Analytical Reagent Grade benzene by the method described in Chapter 4, and this uniform benzene stock used for further experiments is henceforth called pure benzene.

Typical yield-relationships for the oxidation of Analytical Reagent Grade benzene and pure benzene are given in Fig. 5.02.

5.2.3 The Effect of Temperature

The effect of changing the temperature from 630°C to 670°C, with
The Predicated Yield from the Kinetic Model
Fig. 5.03

Effect of Temperature - Pure Benzene Case (5.5% O₂ in Feed, .78 Seconds)
Fig. 5.04

The Effect of Temperature on Selectivity
Fig. 5.05

Effect of Contact Time, Pure Benzene at 650°C, 5.5% O₂ in Feed
Fig. 5.06

The Effect of % Oxygen in Feed on Product Yield - Pure Benzene Case, 650°C, .78 seconds
Fig. 5.07

Effects of oxygen concentration on conversion and selectivity - Pure Benzene Case (650°C, .78 Sec. Time)
5.5% oxygen in the feed and .78 contact time is shown in Fig. 5.03. The quantities of carbon dioxide are expressed as mole % benzene converted to these products, unless otherwise mentioned.

As the temperature is raised, the rate of diphenyl formation increases faster than that of phenol. The relationship between percentage of benzene converted to CO and CO₂ and temperature (Figs 5.01 and 5.03) indicates that the products are possibly formed by a side reaction which could be a surface effect.

Fig. 5.04 shows that the selectivity increases with temperature from 14.6% at 630°C to 29.0% at 670°C, despite a decrease in the phenol/diphenyl ratio because CO/CO₂ formation does not increase to a great extent with the rise in the temperature. The conversion rises from 0.5 to 1.91% in the same temperature range.

But due to decrease in the phenol/diphenyl ratio at higher temperatures, a maximum in the selectivity curve (Fig. 5.04) is likely to occur at a value in the range of 35-45%.

5.2.4 Comparison with the Literature Data

Norrish and Taylor (62) carried out experiments with pure benzene at 685°C. It is interesting to note that extrapolation of the selectivity curve (in Fig. 5.04) gives us a selectivity of 36% at 685°C, a value very close to those obtained by Norrish and Taylor (30-35%).

5.2.5 Contact Time

A typical relationship between product yield and contact time is shown in Fig. 5.05. Although phenol/diphenyl ratio decreases with increase in contact time, the overall selectivity increase is mainly due to the low rate of increase of the combustion reactions.

5.2.6 Oxygen Concentration in Feed

Phenol and carbon dioxide formation increases with increasing oxygen percentage in the feed, while diphenyl formation shows a...
slightly downward trend (Fig. 5.06). Selectivity shows a maxima at 2% oxygen in the feed, while phenol/diphenyl ratio rises with increasing concentration of oxygen (Fig. 5.07). Selectivity is not found to be very sensitive to oxygen concentration above 2% in the feed.

5.3 Discussion and the Basis for Reaction Mechanism for the Oxidation of Pure Benzene

For the construction of a mechanism (Chapter 6) to fit the data on pure benzene oxidation, it will be assumed that:

Combustion reaction resulting in the formation of the oxides of carbon at such low conversions is a parallel reaction not related to any degradation of phenol or diphenyl.

Further, the mechanism involved in phenol and diphenyl formation is exclusive and not interfered with to any great extent by CO/CO₂ formation. Combustion possibly takes place at the surface, while phenol and diphenyl are the results of homogeneous reactions.

A kinetic model for pure benzene oxidation should conform to the following observations:

1. The diphenyl formation rate is more sensitive to temperature than phenol formation rate, and hence requires a higher activation energy.

2. The phenol formation rate is dependent on the oxygen concentration in the feed, while the diphenyl formation rate is independent of it.

5.4 The Promoted Oxidation of Benzene

The experiments with chloroform as promoter were carried out in the following range of operating conditions:

Temperature - 580-630°C
% Oxygen in Feed - 1 to 10%

Contact time - .4 to 1.1 seconds

Chloroform content - 1% weight of benzene

1% weight concentration of promoter was used for the experiments because such a concentration gave the maximum possible conversion of benzene over the temperature range without major loss in phenol selectivity. Higher concentration of chloroform resulted in the formation of dark carbonaceous products.

A temperature range lower than that employed for the pure benzene oxidation (630-670°C) was used for the oxidation with a promoter because:

1. Substantial yields of phenol (0.4 to 1.4%) and benzene conversion (.5 to 3%) could be obtained at the temperature range of 590-630°C.

2. At temperatures of 640-650°C, there was an abrupt rise in the formation of oxides of carbon and heavy carbonaceous substances (pitch) were detected in the liquid sample in considerable quantities.

The products formed in the oxidation with a promoter were similar to those obtained with pure benzene, i.e. phenol, diphenyl, carbon monoxide, carbon dioxide and water, with traces of maleic acid, naphthalene, catechol and diphenyl ether. Hydrochloric acid is also formed, due to decomposition of the chloroform and it accounted for 70-85 mole % of the chloroform decomposed. Some of the carbon associated with the chloroform probably forms carbon oxides, but in the present study all oxides of carbon have been attributed to benzene decomposition in order to avoid underestimation of the benzene conversion. Chloroform conversion has been accounted for separately by measuring its concentration in the feed and the product streams. A typical calculation on yields and conversions is presented in Table 4.02 (Chapter 4).
5.5 Observations on the Experimental Results: Promoter Case

5.5.1 The Effect of Temperature

The effect of temperature on the yield and selectivity of the products for the promoted oxidation is presented in Fig. 5.08 together with the temperature effect on the oxidation of pure benzene for comparison. The following points are worth noting:

1. When the promoter is used, the increase in yield of both phenol and diphenyl is nearly tenfold, compared to the pure benzene oxidation at a temperature of 630°C (Fig. 5.08).

2. There is no improvement in the phenol/diphenyl ratio (1.05) for the promoter case, compared with the pure benzene case at a temperature of 630°C. However, the phenol/diphenyl ratio is increased to 3.2 by lowering the temperature to 585°C and using the promoter. Thus the improvement in selectivity with the use of promoter could be attributed to the reaction being initiated at lower temperatures than that for pure benzene oxidation.

3. Despite a sharp rise in the phenol and diphenyl yield with the use of the promoter, the yield of the oxides of carbon show very little increase compared with their yield on the oxidation of pure benzene, up to a temperature of 630°C. This confirms our earlier hypothesis that combustion of phenol to oxides of carbon was negligible at lower temperatures. However, above a temperature of 630°C combustion of phenol appears to be taking place.

A maximum selectivity of 69% for phenol at a conversion of 0.8% (585°C) could be obtained.
The Effect of Temperature on Benzene Oxidation

Fig. 5.08

Chloroform as Promoter
- Phenol
- Diphenyl
- CO & CO₂

Pure Benzene
- Phenol
- Diphenyl
- CO & CO₂
Fig. 5.09

The Effect of Temperature on Phenol Selectivity and Conversion on Oxidation with Promoter
Effect of Contact Time (630°C, 1% CHCl₃, 5.5% O₂ in Feed)
Fig. 5.11
The Effect of Contact Time on Benzene Conversion and Phenol Selectivity at 630°C
Fig. 5.12

Effect of % O₂ in Feed on Product Yields (1% CHCl₃, .75 sec., 630°C)
The Effect of $O_2\%$ in Feed ($1\%$ CHC$_3$, 630$^\circ$C)

Fig. 5.13

$%\text{Oxygen in Feed} 
\begin{array}{c}
\text{Selectivity} \\
0 & 2 & 4 & 6 & 8 & 10 & 12 \\
\hline
\end{array}$

$%\text{Oxygen in Feed (1\% CHC$_3$, 630$^\circ$C)}$ 

Fig. 5.14

$%\text{Oxygen in Feed Giving the Maximum Selectivity for Phenol}$
5.5.2 The Effect of Contact Time

A typical yield-time relationship (630°C, 5.5% oxygen in feed) is presented in Fig. 5.10. There is a decrease in selectivity for phenol from 44% to 36% (Fig. 5.11) as conversion is raised from 1.1 to 2.9% by increasing the contact time.

5.5.3 The Effect of Oxygen Concentration in the Feed

The yields of phenol, diphenyl and oxides of carbon increase with the increase in oxygen concentration in the feed (Fig. 5.12). It is interesting to note that in the pure benzene oxidation, diphenyl yield was not very sensitive to oxygen concentration and decreased with increasing amount of oxygen in the feed, unlike the present case.

The selectivity for phenol rises with the increase in the initial oxygen concentration up to 7% oxygen in feed at 630°C (Fig. 5.13) and decreases at oxygen concentrations above 7%. The oxygen concentration in the feed corresponding to the maximum selectivity varies with the temperature, going up to 11.0% on lowering the temperature to 585°C (Fig. 5.14).

5.5.4 Promoter Consumption

The promoter conversion was found to increase with increasing severity of the reaction or degree of benzene conversion, going up to 70% at 630°C from 10-20% at 585°C, on its initial concentration.

Assuming that the chloroform decomposition is the main initiating reaction and diphenyl formation is the main termination reaction, it was decided to find if there was any relationship between chloroform consumption as percentage of the amount of chloroform reacted per mole benzene feed, and diphenyl yield. The data, although scattered, shows an approximately straight line relationship (Fig. 5.15).

5.6 Discussion and the Basis for Reaction Mechanism for Benzene Oxidation in Presence of Chloroform as Promoter

The assumptions made for the construction of a reaction mechanism
Fig. 5.15

Promoter Consumption Related to the Diphenyl Yield
and the experimental observations that should be satisfied by the mechanism are:

1. Reactions leading to the formation of oxides of carbon are regarded as parallel reactions not interfering with the phenol and diphenyl forming reactions, as in the case of pure benzene (Section 5.3). This assumption is valid within the limits of a maximum temperature of 630°C and maximum oxygen content of 7.0% in the feed.

2. The initiation reactions below 630°C are attributed only to the decomposition of chloroform (Section 5.5.1).

3. As there is little improvement in selectivity compared with the pure benzene case for the same conditions of temperature, the role of the promoter as an oxygen carrier for the phenol forming reactions must be negligible (Section 5.5.1).

4. Since diphenyl formation is a termination reaction (Section 2.4.4), the increase of diphenyl yield with increased concentration of oxygen (Section 5.5.3) indicates that oxygen has a role to play in the initiation reaction.

5.7 Pyrolysis of Benzene

To check some of the postulations in sections 5.3 and 5.6, a few experiments on the pyrolysis of benzene were carried out with and without chloroform as promoter, but in the absence of any oxygen.

The diphenyl yield obtained on pyrolysis at three different temperatures with 0.78 sec. contact time is shown in Fig. 5.16 as points, together with the curves for diphenyl yield with 5.5% oxygen in the feed, with and without the promoter. The results indicate that above 630-640°C initiation of phenyl radicals with pure benzene could take place without oxygen or promoter. However, below 630°C, the promoter has a major role.
(1) Diphenyl Yield with 5.5% Oxygen & 1% weight Chloroform
(2) Diphenyl Yield with 5.5% Oxygen & 0.0% weight Chloroform
Pyrolysis with 1.0% weight Promoter
Pyrolysis with 0.0% weight Promoter

Fig. 5.16

Results on the Pyrolysis of Benzene
in the initiation of phenyl radicals and the effect of the promoter is considerably enhanced by the presence of oxygen.
CHAPTER 6

Development of the Kinetic Model and treatment of the Experimental Data
CHAPTER 6

Development of the Kinetic Model
and Treatment of the Experimental Data

6.1 The Kinetic Model for a Complex Reaction

The rate of an elementary reaction of the type $A + B \rightarrow \text{Products}$, is normally expressed in an explicit form -

$$r = K C_A^a C_B^b \quad (i)$$

Where $r$ is the rate of formation of a product, $C_A$ and $C_B$ are the concentrations of the reactants $A$ and $B$, $a$ and $b$ are the order of the reaction with respect to $A$ and $B$ respectively and $K$ is the rate constant.

But with a complex reaction, such an expression has limited applicability, since the order of the reaction with respect to each of the reactants might change, due to changes in the rates of elementary steps with different process conditions. Besides, such an expression reveals very little about the mechanism of the process.

A complex reaction can be expressed as a series of elementary reactions, the rate of the $j$'th reaction being:

$$r_j(C) = K_j r_j(C) \quad (ii)$$

Where $K_j$ is the rate constant of the $j$'th reaction and $C$ is the concentration vector of the species in the system (77). $K_j$ is the unknown factor.

The rate of production of the $i$'th chemical species is then given by:

$$r_i^p(C) = \sum_{j=1}^{n_j} \alpha_{ij} r_j(C) \quad (iii)$$

Where $\alpha_{ij}$ is the stoichiometric coefficient of the $i$'th species in the $j$'th reaction.

The concentration of the $i$'th species at time $t$ is given by:

$$C_i^t = C_i^0 + \int_0^t r_i^p(C) \, dt \quad (iv)$$

Where $C_i^0$ is the initial concentration.
If the concentrations of the species in the experimental samples at time $t_p$, where $p = 1, 2, 3, \ldots, n_p$ ($n_p$ being the number of samples), are termed $C_i^p$ and the concentrations at time $t_p$ computed from equation (iv) are termed $C_i^{\text{comp}}$, then the error between the computed values and experimental values of concentrations can be defined by the function:

$$e = f(C_i^p, C_i^{\text{comp}})$$

(v)

The best values of $K_j$ (equation ii) will be those for which 'e' is minimum. A suitable optimisation procedure may be used to minimise 'e', by varying the rate constants, $K_j$, for each elementary reaction. Such a model would show us the importance of each elementary reaction under different conditions of temperature and concentrations of the chemical species.

The Rosenbrock Hill Climbing method (78, 79) was used in the present work for minimisation of the error function. The method can be used for the optimisation of a function containing any number of variables from 1 to 20, and has been found suitable for the evaluation of rate constants by the procedure described in this section (77). The Rosenbrock Hill Climbing method is available as a computer subroutine in the university computer centre.

The error function (equation v) for the optimisation (minimisation) procedure was defined as:

$$e = (1 - \frac{C_i^p}{C_i^{\text{comp}}})^2$$

(via)

In reactions involving free radicals, the differential equations expressing the rates of free radical ($R_\cdot$) formation, are simplified by the conventional assumption of the stationary free radical concentration:

$$\frac{d R_\cdot}{dt} = 0$$

(vii)
This concept is valid in most free radical reactions, when the concentrations of the free radicals are very small compared with those of the stable intermediates and products. R. H. Snow (80) has referred to the criteria for the validity of such a concept in mathematical terms. However, in the present work, we shall consider the free radical concept to be applicable and examine its validity from the analysis of the results.

Due to the number of free radicals involved, very complex expressions are often obtained for the term under the integral sign in equation (iv). Such expressions are difficult to integrate explicitly. R. H. Snow et al (81) in their computer study on ethane pyrolysis have avoided such problems by using numerical integration methods.

The strategy followed in the present work for the treatment of the kinetic data is outlined in the following steps:

1. Consideration of all the possible elementary reactions and elimination of the less likely ones by analyzing the literature data (Chapter 2).

2. Consideration of the energetics of the elementary reactions and further elimination if possible.

3. Listing of the likely sequence of elementary reactions with preliminary estimates of their rate constants.

4. Equating the rates of change of free radical concentration for each radical to zero, resulting in 'n'. Simultaneous equations for 'n' radicals and determination of the free radical concentrations by solving the equations.

5. Development of a computer model with the order of instructions given in Fig. 6.01.

From the value of the minimised error function (e) (Fig. 6.01), the standard error of estimate can be estimated as:

\[ s = e^{0.5} \left( \frac{N - n}{N} \right)^{0.5} \]  

where, e = the value of minimised error function (equation viii), N = number of data points, n = number of variables, rate constants in this case.
INPUT: (1) Initial Concentration of reactants and products.
(2) Experimental data: product conc. at different contact times
(3) Initial estimates of the rate constants.
(4) Chosen value of time differential (dt) for numerical integration.

Find reaction rate and product concentration after a single differential time (equation iv)

Repeat for successive differential times to find the computed product conc. at time $t_p$

Evaluate error function (eqn. via) from the computed and experimental values.

Rosenbrock Hill-Climbing Procedure

Is the error function minimised? No

OUTPUT: Final values of rate constants, computed product concentrations & error

Fig. 6.01
The scheme for the rate constant evaluation program.
6.2 Energetics of the Elementary Reactions

The Arrhenius Equation expresses the rate constant as:

\[ K = A_o e^{-E/RT} \]  

Where \( A_o \) is the frequency factor and \( E \) is the activation energy for the reaction.

Considerable data is available in literature (82-86) regarding the energetics of the free radical reactions. However, the phenyl radical and non-hydrocarbon radicals formed by it (e.g. phenoxy radical) are among the least studied ones and data regarding them is scarce.

Activation energies of the elementary reactions have been estimated, wherever data is not available, according to the following generally accepted rules:

1. Activation energy of unimolecular dissociation reactions is equivalent to the dissociation energy of the bond being broken (82), i.e. for \( AB \rightarrow A + B \).

\[ E = Q(A-B) \]  

2. Activation energy of free radical combination (opposite of reaction ix) is zero.

3. For exchange reactions (83):

\[ A + BC \rightarrow ABC \rightarrow AC + B + Q_R \]  

the activation energy can be found in the following ways:

\[ E = \Delta H_{f}^{ABC} - \Delta H_{f}^{A} - \Delta H_{f}^{BC} \]  

Where \( ABC \) is the transition state molecule and \( H_f \) is the heat of formation at 298°K (84).

If \( Q_R \) is exothermic (86),

\[ E = 0.05 \cdot Q_{(A-C)} \]  

where \( Q_{(A-C)} \) = bond energy of AC.

If \( Q_R \) is endothermic, the heat of reaction should be added to \( E \).
### Table 6.01
Heats of Formation and Bond Dissociation Energies

<table>
<thead>
<tr>
<th>Compound or Free Radical</th>
<th>Heat of Formation KCal at 25°C</th>
<th>Bond Dissociation Energy, KCal</th>
<th>Comment &amp; Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_6$</td>
<td>19.8</td>
<td></td>
<td>(48)</td>
</tr>
<tr>
<td>$C_6H_5 - H$</td>
<td>99.7</td>
<td></td>
<td>(48)</td>
</tr>
<tr>
<td>$C_6H_5^*$</td>
<td>67.5</td>
<td></td>
<td>(48)</td>
</tr>
<tr>
<td>$C_6H_5 - OH$</td>
<td>-24.0</td>
<td>99.5</td>
<td>Estimated</td>
</tr>
<tr>
<td>$C_6H_5 - C_6H_5$</td>
<td>94.5</td>
<td></td>
<td>Estimated</td>
</tr>
<tr>
<td>O$^•$</td>
<td>59.0</td>
<td></td>
<td>(85)</td>
</tr>
<tr>
<td>H$^•$</td>
<td>52.0</td>
<td></td>
<td>(86)</td>
</tr>
</tbody>
</table>

### Table 6.02
Activation Energies (Estimated)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation Energy KCal/ Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_6 \rightarrow C_6H_5^* + H^•$</td>
<td>99.7</td>
</tr>
<tr>
<td>$C_6H_5^* + O_2 \rightarrow C_6H_6OO^•$</td>
<td>5.0</td>
</tr>
<tr>
<td>$C_6H_5O^• + C_6H_6 \rightarrow C_6H_5^* + C_6H_5CH$</td>
<td>15.0</td>
</tr>
<tr>
<td>$C_6H_5OO^• + C_6H_6 \rightarrow C_6H_5O^• + C_6H_5OH$</td>
<td>49.0</td>
</tr>
<tr>
<td>$C_6H_5^* + C_6H_5^• \rightarrow C_{10}H_{10}$</td>
<td>0.0</td>
</tr>
</tbody>
</table>
4. For the exchange reaction (87) -

$$\text{AB} + \text{CD} \rightarrow \text{AC} + \text{BD} + Q_R \quad \text{(exothermic)} \quad \text{(xiv)}$$

$$E = 0.28 \left( Q_{A-B} + Q_{C-D} \right) \quad \text{(xv)}$$

For the endothermic reaction (reverse), the heat of reaction should be added to the above.

Estimation of the activation energy involves knowledge of heats of reaction, heats of formation and bond dissociation energies. Wherever literature data is not available, estimations of the heats of formation for molecules as well as free radicals have been made on the basis of the method of group contributions developed by Franklin (85, 86). Franklin's method is expressed mathematically as:

$$H_f^o = \Delta H_{gi} + \Delta H_{g\cdot} + R \quad \text{(xvi)}$$

Where $H_{gi}$ is the heat contribution attributed to the '$i$'th group, $H_{g\cdot}$ is the group equivalent value for the groups to which an unpaired electron is assigned and $R$ is the resonance energy. Tabulated values of many hydrocarbon as well as non-hydrocarbon groups are reported. The energetics of the radicals and reactions are tabulated in Tables 6.01 and 6.02.

6.3 Pure Benzene Case (Model 1)

On the basis of the earlier observations (sections 2.4 and 5.3), the mechanism of phenol and diphenyl formation can be described through the following free radical chain involving phenoxy radicals.

$$\text{C}_6\text{H}_6 \xrightarrow{K_1} \text{C}_6\text{H}_5\cdot + \text{H}\cdot \quad \text{(xvii)}$$

$$\text{C}_6\text{H}_5\cdot + \text{O}_2 \xrightarrow{K_2} \text{C}_6\text{H}_5\text{OO} \cdot \quad \text{(xviii)}$$

$$\text{C}_6\text{H}_5\text{OO} \cdot + \text{C}_6\text{H}_6 \xrightarrow{K_3} \text{C}_6\text{H}_5\text{O} \cdot + \text{C}_6\text{H}_5\text{OH} \quad \text{(xix)}$$

$$\text{C}_6\text{H}_5\text{O} \cdot + \text{C}_6\text{H}_6 \xrightarrow{K_4} \text{C}_6\text{H}_5\cdot + \text{C}_6\text{H}_5\text{OH} \quad \text{(xx)}$$

$$\text{C}_6\text{H}_5\cdot + \text{C}_6\text{H}_5\cdot \xrightarrow{K_5} \text{C}_{12}\text{H}_{10} \quad \text{(xxi)}$$
Assuming that the stationary free radical concept holds for the system, we can write the following rate expressions:

\[
\frac{d(C_6H_5\cdot)}{dt} = K_1(C_6H_6) - K_2(C_6H_5\cdot)(O_2) \quad (\text{xxii})
\]

\[+ K_4(C_6H_5\cdot)(C_6H_6) - K_5(C_6H_5\cdot)^2 = 0 \quad (\text{xxiii})
\]

\[
\frac{d(C_6H_5OO\cdot)}{dt} = K_2(C_6H_5\cdot)(O_2) - K_3(C_6H_5\cdot)(C_6H_6) = 0 \quad (\text{xxiv})
\]

Solving the above equations, we can express the free radical concentrations as:

\[
(C_6H_5\cdot) = \frac{K_1}{K_5} (C_6H_6)^{0.5} \quad (\text{xxv})
\]

\[
(C_6H_5OO\cdot) = \frac{K_2}{K_3} \left( \frac{K_1}{K_5} \right)^{0.5} \frac{(O_2)}{(C_6H_6)^{0.5}} \quad (\text{xxvi})
\]

\[
(C_6H_5O\cdot) = \frac{K_4}{K_5} \left( \frac{K_1}{K_5} \right)^{0.5} \frac{(O_2)}{(C_6H_6)^{0.5}} \quad (\text{xxvii})
\]

The rates of product formation are, then, given by the equations:

\[
\frac{d(C_6H_5\cdot)}{dt} = K_3(C_6H_5\cdot)^2 = K_1(C_6H_6) \quad (\text{xxviii})
\]

\[
\frac{d(C_6H_5OH)}{dt} = K_3(C_6H_5\cdot)(C_6H_6) + K_4(C_6H_5\cdot)(C_6H_6)
\]

or \[
\frac{d(C_6H_5OH)}{dt} = 2K_2 \left( \frac{K_1}{K_5} \right)^{0.5} (C_6H_6)^{0.5} (O_2) \quad (\text{xxix})
\]

6.4 Comments on Model 1

Before proceeding further, the following observations regarding the above model are put forward.
1. For low conversions of benzene, the benzene concentration term \((C_6H_6)\) may be treated as a constant throughout the reaction period. In such a case, the product formation rates are independent of reaction rate constants \(K_3\) and \(K_4\). Only if benzene concentration is taken as a variable, the above rate constants come into consideration.

2. It is a semi-empirical model and does not take into account the mechanism of carbon dioxide formation.

3. It does not include any degenerate branching reaction. It is not essential that degenerate branching should take place during the phenol formation step. The degenerate branching may take place by branching of alkanes or alkenes in a separate set of reactions resulting from the rupture of the benzene ring at the reactor wall or otherwise.

4. Since the model is based on assumption of stationary radical concentration, it cannot take into account the unsteady state of the induction period. It is therefore preferable not to take zero time as the initial state for integrating the rate expressions.

5. The model agrees qualitatively with our experimental observations, summarised in Section 5.3. The rate constant \(K_1\) in equations xxviii and xxix - which is the rate constant for the dissociation of a hydrogen atom from the benzene molecule - has a very high activation energy component (100,000 cal/mole, Table 6.02). While the rate of phenol formation is proportional to the square root of \(K_1\), the diphenyl formation rate is directly proportional to \(K_1\). This aptly explains increasing of phenol/diphenyl ratio with the lowering of temperature (Section 5.3).
6.5 *Kinetic Treatment of the Data (Pure Benzene Oxidation)*

The rates of phenol and diphenyl formation can be expressed as:

(equations xxviii and xxix)

\[
\frac{d(C_{6}H_{5}OH)}{dt} = K' (C_{6}H_{6})^{5}(O_{2})^{2} \tag{xxix.a}
\]

\[
\frac{d(C_{12}H_{10})}{dt} = K_{1} (C_{6}H_{6}) \tag{xxviiia}
\]

where \( K' = 2 K_{2} \sqrt{\frac{K_{1}}{K_{5}}} \)

Taking into account the Arrhenius equation for rate constants -

\[
K_{i} = A_{i} e^{-E_{i}/RT}
\]

the above expression can be written as -

\[
K' = 2 A_{2} \left( \frac{A_{1}}{A_{2}} \right)^{5} e^{-(E_{1}/2 + E_{2})RT} \approx A' e^{-E/RT} \tag{xxx}
\]

The value of \( E \) is given by -

\[
E = E_{1}/2 + E_{2} + E_{5}
\]

the subscripts referring to the corresponding elementary reaction. \( E_{5} \), being the activation energy of combination of phenol radicals, should be equal to zero.

\[
\therefore E = E_{1}/2 + E_{2} \tag{xxxii}
\]

The rate constant of diphenyl formation is given by -

\[
K_{1} = A_{1} e^{-E_{1}/RT} \tag{xxxiii}
\]

From the experimental data at different temperatures, \( K' \) and \( K_{1} \) at those temperatures were estimated using the procedure described in Section 6.1. A flow diagram of the computer programme (Fig. 6.01) used for the evaluation of the rate constants at a particular temperature is given in Fig. 6.01. From 2.3 log \( K_{i} \) versus \( \frac{1}{T} \) relationship, \( A_{i} \) and \( E_{i} \) values were estimated (Fig. 6.02). The values of \( K \) and \( K' \) for various temperatures are reported in Table 6.03.
Fig. 6.02

Arrhenius Plot for Rate Constants of Phenol and Diphenyl Formation
Fig. 6.03

Experimental Yields (Points) and Predicted Yields (Firm Lines) of Phenol and Diphenyl at 650°C from Pure Benzene in terms of mole/cc concentration.
The Predicted Yields from the Kinetic Model (5.5 x 0.5 in feed)
Use of the above data (Fig. 6.02) and equations xxx, xxxi and xxxii, give the following values of activation energies ($E_i$) and pre-exponential factors:

\[
E = 60.2 \text{ KCal/mole}, \quad A' = 2.88 \times 10^{15} \\
E_1 = 97.0 \text{ KCal/mole}, \quad A_2 \frac{A_1}{A_5} = 1.44 \times 10^{15} \\
E_2 = 12.7 \text{ KCal/mole}, \quad A_1 = 5.05 \times 10^{19}
\]

**Discussion**

The calculated values of $E_1$ and $E_2$ compare well with the estimated and literature values given in Table 6.01, which are:

$E_1 = 100 \text{ KCal/mole}$ and $E_2 = 5 \text{ KCal/mole}.$

While the value of $E_1$ is established by experimental investigation (48), the value of $E_2$ is not very well established. I. I. Ioffe (69) estimated its value at 13.5 KCal/mole.

The concentration-time plots for the predicted results along with experimental results are given in Figs 6.03 and 6.04. The predicted results agree with the experimental results with a standard error of estimate within 10%, according to the definition of this error given in Section 6.1 (equation vib).

On the basis of the above estimates, the rates of phenol and diphenyl formation with pure benzene as chargestock can be written as:

\[
\frac{d(C_{6}H_{5}OH)}{dt} = 2.88 \times 10^{15} \times e^{-\frac{30,100}{T}} \times (O_2)(C_{6}H_5)^5 \quad (xxxiii)
\]
6.6 The Mechanism and Kinetic Model for the Promoted Oxidation of Benzene

On the basis of the experimental results on the oxidation of benzene in the presence of chloroform as promoter (Section 5.6), and the observations on the pyrolysis of benzene (Section 5.7), it is obvious that the reaction is initiated mainly by the chloroform decomposition. The effect of chloroform was found to be enhanced by the presence of oxygen. The initiation reactions could be written as:

\[
\begin{align*}
\text{(xxxv)} & : & \text{CHCl}_3 & \rightarrow & \text{CHCl}_2^- + \text{Cl}^- \\
\text{(xxxvi)} & : & \text{CHCl}_3 + \text{O}_2 & \rightarrow & M^+ + \text{Cl}^- 
\end{align*}
\]

where \( M^+ \) is an oxygenated complex.

The experimental observations (Section 5.6) indicate that the role of \( M^+ \) as an oxygen carrier for phenol forming reactions is minimal.

Chloroform is also known to decompose to form a biradical (48):

\[
\begin{align*}
\text{(xxxvii)} & : & \text{CHCl}_3 & \rightarrow & \text{Cl}^- + \text{HCl} 
\end{align*}
\]

Shilov (87) studied the decomposition of chloroform in the presence of toluene and found that the decomposition temperature of chloroform was above 600°C, the main products being HCl, CH\(_4\) and C\(_2\)H\(_6\). Thus, reaction (xxxvi) is probably the major reaction in the initiation step.

\( M^+ \) may further decompose to generate further radicals and combustion products:

\[
\begin{align*}
\text{(xxxviii)} & : & \text{M}^+ & \rightarrow & \text{Cl}^- + \text{HCl} + \text{Carbon oxides} 
\end{align*}
\]

The Cl\(^-\) and M\(^+\) free radicals generated initially react with the benzene molecule to form phenyl radicals:

\[
\begin{align*}
\text{(xxxix)} & : & \text{Cl}^- + \text{C}_6\text{H}_6 & \rightarrow & \text{C}_6\text{H}_5^- + \text{HCl} 
\end{align*}
\]
The propagation reaction is considered to be through the formation of phenoxy radicals, in keeping with our observation on the literature information (Section 2.4) and the interpretation of the data on the pure benzene oxidation (Section 6.4):

\[ \text{M}^* + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5^* + \text{M}^* \]  
(xl)

The development of rate equations according to the method described in Section 6.1 incorporating all the reactions mentioned in this section, leads to complex expressions. Considering only equation (xxxvi) as the initiation step, and the reactions (xxxix) and (xviii) to (xxi) as the phenol and diphenyl forming reactions, the derived rate expressions were:

\[ \frac{d(\text{C}_6\text{H}_5\text{OH})}{dt} = 2K_2 \left( \frac{K_5}{K_5^*} \right) \text{C}_6\text{H}_3\text{O} \text{H} \left( \text{CHCl}_3 \right)^5 \left( \text{O}_2 \right)^{1.5} \]  
(xli)

\[ \frac{d(\text{C}_6\text{H}_4\text{Cl})}{dt} = K_6 \left( \text{CHCl}_3 \right) \left( \text{O}_2 \right) \]  
(xlii)

\[ \frac{d(\text{CHCl}_3)}{dt} = K_6 \left( \text{CHCl}_3 \right) \left( \text{O}_2 \right) \]  
(xliii)

Equations (xli) to (xliii) did not give a good fit to the experimental data. Obviously, they accrue from a very simplified version of the role of the promoter - for example, equation (xxxvi) explains the dissociation of only one chlorine atom from the chloroform molecule.

It was decided to correlate the data empirically for use in process optimisation (Chapter 7). A kinetic model involving numerical integration of the rate with respect to contact time was found to involve a considerable computation time (15-20 minutes), without any particular gain in accuracy. So it was decided to express the yield of products
in the present case as a function of time, besides reactant concentration (mainly oxygen, benzene concentration being assumed constant). The empirical relationships used were:

\[ Y_{\text{Ph}} = K_{\text{Ph}} (\text{contact time})^{X_1} \left( \text{Oxygen in feed} \right)^{X_2} \] (xliv)

\[ Y_{\text{DPh}} = K_{\text{DPh}} (\text{contact time})^{X_3} \left( \text{Oxygen in feed} \right)^{X_4} \] (xlv)

\[ Y_{\text{comb}} = K_{\text{comb}} (\text{contact time})^{X_5} \left( \text{Oxygen in feed} \right)^{X_6} \] (xlvi)

where,

\( Y_{\text{Ph}} \) = moles of benzene converted to phenol per 100 moles of benzene per pass

\( Y_{\text{DPh}} \) = moles of benzene converted to diphenyl per 100 moles of benzene per pass

\( Y_{\text{comb}} \) = moles of benzene converted to CO and \( \text{CO}_2 \) per 100 moles of benzene per pass

\( X_1 \ldots X_6 \) = factors giving the best fit of the data

\( K_{\text{Ph}}, K_{\text{DPh}}, K_{\text{comb}} \) = functions of temperature

The values of \( X_1 \)'s and \( K \)'s giving the best fit for the data (Set , Appendix 4) are presented in Table 6.05

### Table 6.05

<table>
<thead>
<tr>
<th>Temp°C</th>
<th>( X_1 )</th>
<th>( X_2 )</th>
<th>( X_3 )</th>
<th>( X_4 )</th>
<th>( X_5 )</th>
<th>( X_6 )</th>
<th>( K_{\text{Ph}} )</th>
<th>( K_{\text{DPh}} )</th>
<th>( K_{\text{comb}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>585</td>
<td>.920</td>
<td>.830</td>
<td>.930</td>
<td>.790</td>
<td>.913</td>
<td>.530</td>
<td>.125</td>
<td>.040</td>
<td>.045</td>
</tr>
<tr>
<td>610</td>
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<td>.980</td>
<td>.805</td>
<td>.940</td>
<td>.570</td>
<td>.123</td>
<td>.120</td>
<td></td>
</tr>
<tr>
<td>630</td>
<td>.986</td>
<td>.750</td>
<td>1.010</td>
<td>.810</td>
<td>.976</td>
<td>.602</td>
<td>.307</td>
<td>.235</td>
<td>.230</td>
</tr>
</tbody>
</table>

112
The consumption of chloroform expressed as moles of chloroform decomposed per 100 moles of benzene feed per pass was correlated to diphenyl yield (moles of benzene converted to diphenyl per 100 moles benzene per pass) according to the straight line equation (vide Fig. 5.15):

\[ Y_{\text{CHCl}_3} = 0.03 + 0.405 \times Y_{\text{Dph}} \]  

(xlvii)
CHAPTER 7

Economic Optimisation of the Process
CHAPTER 7

Economic Optimisation of the Process

7.1 Summary of the Optimisation Procedure

As described in Chapter 1 (Section 1.5), a set of mathematical equations describing the economics of the process as a function of the process variables (mainly temperature, contact time and oxygen percentage in feed), was used for the optimisation of the process. The procedure consists of the following steps:

1) A flowsheet was developed for a process to manufacture 20,000 tons/year of phenol, with air or oxygen as the oxidising medium (Fig. 7.01).

2) Design equations were developed relating the size of the major items of equipment for various conditions of material balance (dependent mainly on phenol yield), temperature and air or oxygen content in the feed. The design methods used are briefly described in Appendix 5.

3) Cost of equipment was calculated for various values of process conditions, using cost equations available in literature (Appendix 5, Table A5.03).

4) The cost of the major equipment was correlated graphically with the process variables on the basis of the size and cost relationships of Sections (2) and (3) above: \( \text{Cost of equipment} = f(\text{temperature}, \text{oxygen conc.}, \text{phenol yield}) \)

5) The total capital cost was assumed to be 4.0 times the sum of the cost of the major items of equipment.

6) The fixed annual cost for running a plant was regarded as 21% of the capital cost.

7) The costs of utilities (fuel, steam, water and power) were correlated to various values of phenol yield.
The cost of raw material (benzene) is obviously a function of phenol selectivity and was expressed as such.

Steps (6) to (8) lead to a function expressing the cost of phenol production:

\[ C_{ph} = 0.21 \times \text{capital cost} + \text{cost of utilities} \]
\[ + \text{cost of raw material} \]
\[ + \text{cost of promoter} \]
\[ + \text{cost of oxygen} \]
\[ - \text{by-product credit} \]  

or

\[ C_{ph} = f(\text{Phenol yield and selectivity, by-product yield, promoter consumption, temperature, oxygen concentration in feed}) \]

In Chapter 6, on the kinetic model for the process, the yield and selectivity of phenol, by-product yield (diphenyl) and promoter consumption was correlated to temperature, contact time and % oxygen in feed (equations

Thus the cost of phenol, which is the function to be optimised (minimised), could be expressed as:

\[ C_{ph} = f(\text{temperature, contact time, % oxygen in feed, X}) \]  

where X could be a plant design variable.

The cost equations thus obtained are summarised in Appendix 5 (Table A5.04), along with raw material and by-product prices. Cost of utilities are given in Appendix 1.

The cost function was optimised using the Rosenbrock Hill Climbing Method (78, 79). The method is practicable with non-linear equations containing 1 to 20 variables. A computerised procedure for the Rosenbrock Method was available at the University Computer Centre.
Flow Scheme for Benzene Oxidation Process
Yield-selectivity relationship defining phenol cost of £50/ton (Oxygen Case)

Yield-selectivity relationship defining phenol cost of £50/ton (Air Case)

Yield-selectivity data of Lemetre & Caprara (38) with 1% ethanol as promoter

Experimental data, pure benzene

Experimental data with promoter

Economically attractive region of yield & selectivity

Fig. 7.02

The Yield-Selectivity Relationships Defining the Economically Attractive Region
7.2 The Flowsheet

The flowsheet (Fig. 7.01) has been described in Chapter 1 (Section 1.5.1).

Some typical temperature conditions and material balance are presented in Fig. 7.01. For the oxygen case, the amount of oxygen in the feed was taken to be 1.2 times the stoichiometric requirement for the process. It was shown in Chapter 1 (Section 1.5.2) that the use of oxygen was economically more attractive than air for the envisaged process. Hence, optimisation on the basis of oxygen as the oxidising material was carried out for the process data. The design procedure for sizing of the equipment is presented in Appendix 5.

7.3 Preliminary Observations on the Process Optimisation

A preliminary observation on the economics of the experimental data was made by projecting the yield-selectivity relationship obtained by variation of reaction temperature on the economically attractive region of the process defined in Chapter 1 (Fig. 1.08). In Fig. 7.02, the following data is reported, along with the curves defining the economically attractive region:

(1) Experimental data:
   (a) with 1% chloroform as promoter
   (b) with pure benzene

(2) Data of Lemetre and Caprara (38) with 1% ethanol as promoter - used in the preliminary evaluation of the process (Chapter 1).

All three sets of data reflect the effect on selectivity by lowering the yield of phenol (or benzene conversion) through lowering of the temperature. The experimental data is in the region of phenol yield below 1.5% (or benzene conversion below 3.0%), in which the literature data is scarce and extrapolation (dotted line) of the data of Lemetre and Caprara was made for the preliminary evaluation.
It can be seen from Fig. 7.02 that the results obtained with pure benzene are quite discouraging and will not therefore be considered for the optimisation of the process. However, the data obtained with chloroform as promoter falls quite close to the economically attractive region.

It was decided to find the optimum process conditions for the process, using chloroform as promoter, on the basis of the semi-empirical relationships developed in Chapter 6 (Section 6.7). Extrapolation of the yield and selectivity calculations with the semi-empirical correlation was deemed justifiable within reasonable limits.

7.4 Details on the Process Optimisation with the Experimental Data and Using Chloroform as Promoter

The equations reported on the yields of products on the promoted oxidation (equations xliv to xlvi, Section 6.7) are of the type:

\[ \text{Yield} = K_i \text{(contact time)} X_i \times (\% O_2 \text{ in feed}) X_j \]

\( X_i \) and \( X_j \) are found to vary with temperature, to the extent of 10% as the temperature is changed from 630°C to 585°C (Table 6.05, Chapter 6).

It was anticipated that the optimum condition would lie in the lower temperature region, where the selectivity was high. So the values of \( X_i \) and \( X_j \) at 585°C was used for the optimisation purpose. The values of \( K_i \), which are very sensitive to temperature, were extrapolated by fitting them to quadratic equations. The lower temperature limit was kept only 20°C below the lowest temperature in the experimental data (585°C) so that the empirical extrapolation of \( K_i \) values could be justifiable. The set of equations defining yield and selectivity thus obtained are:

\[ Y_{Ph} = K_{Ph} \text{(contact time)} \times 92 \times (\% O_2 \text{ in feed})^{0.83} \]  
\[ (i) \]

\[ Y_{Dph} = K_{Dph} \text{(contact time)} \times 93 \times (\% O_2 \text{ in feed})^{0.79} \]  
\[ (ii) \]

\[ Y_{comb} = K_{comb} \text{(contact time)} \times 913 \times (\% O_2 \text{ in feed})^{0.53} \]  
\[ (iii) \]
Chloroform consumption = \(.03 + .405 Y_{DPh}\) \((v)\)

\[ K_i^T = a_i + b_i T + c_i T^2 \] \((vi)\)

where \(i\) is any of the components and \(T\) is the temperature in °C. The values of \(a_i\), \(b_i\) and \(c_i\) are given in Table 7.01.

**Table 7.01**

<table>
<thead>
<tr>
<th>(K_{Ph})</th>
<th>(a_i)</th>
<th>(b_i)</th>
<th>(c_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.450</td>
<td>0.0015</td>
<td>(2.05 \times 10^{-5})</td>
<td></td>
</tr>
<tr>
<td>(K_{DPh})</td>
<td>-13.806</td>
<td>0.0495</td>
<td>(4.43 \times 10^{-5})</td>
</tr>
<tr>
<td>(K_{comb})</td>
<td>-11.737</td>
<td>0.0424</td>
<td>(3.83 \times 10^{-5})</td>
</tr>
</tbody>
</table>

Cost equations used are reported in Appendix 5, Table A5.04.

The Rosenbrock Hill Climbing Method was used to find the optimum process conditions, as described in Section 7.1. A flowsheet for the optimisation programme is presented in Fig. 7.03.

The limits of the variables within which extrapolations were made are reported in Table 7.02.

**Table 7.02**

<table>
<thead>
<tr>
<th></th>
<th><strong>Lower Limit</strong></th>
<th><strong>Upper Limit</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp. °C</strong></td>
<td>Experiment</td>
<td>Optimisation</td>
</tr>
<tr>
<td></td>
<td>585</td>
<td>565</td>
</tr>
<tr>
<td>% (O_2) in Feed</td>
<td>1.0</td>
<td>.5</td>
</tr>
<tr>
<td>Contact time</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>(sec.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T) = difference between reaction temp. and pre-heated feed temp. (Fig. 7.01)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 7.0
The scheme for the process optimisation program.

START

Initial values of
Temperature, contact
time and oxygen con-
centration.

Calculate yield and
selectivity of phenol
and reactant conver-
sion (eqns ii-vi, section 7.4)

Estimate the cost of
phenol production
(equations in appendix
V, table A5.04)

Rosenbrock
Hill-climbing
Procedure

Is
the minimum cost
achieved?

No

New estimates
for optimum
temperature, con-
tact time and
oxygen conc.

OUTPUT: Temperature,
contact time, oxygen
conc. (optimum values),
and corresponding
phenol yield & cost.
Only the oxygen case was considered as the air case was found to be less attractive (Chapter 1).

7.5 The Optimum Process Conditions

The minimum costs of phenol production given by the optimisation programme are at the following process conditions:

- Temperature = 565°C
- % O₂ in feed = 7.0%
- Contact time = 6.0 seconds
- Reactor exit temperature = 535°C

It is interesting to note that the optimum falls on the extrapolated region of process conditions.

Corresponding yields and phenol cost are:

<table>
<thead>
<tr>
<th></th>
<th>Yield</th>
<th>Selectivity</th>
<th>Cost, £/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>1.33</td>
<td>76.0</td>
<td>47.05</td>
</tr>
<tr>
<td>Diphenyl</td>
<td>.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combustion gases</td>
<td>.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion</td>
<td>1.78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The cost of phenol at this optimum condition is commercially competitive. However, since it is in the extrapolated region, the kinetics of the process in the indicated process conditions need to be studied.

The present apparatus was not used for studies at such high contact time as the pump (Fig 4.01, Chapter 4) was unsuitable for pumping at low flow rates.

The main conclusion of the process optimisation programme is that the process should be investigated at a temperature as low as possible, and contact time as high as possible.

The optimum yield within the range of experimental work was 0% phenol with 69.0% selectivity (at 565°C and 7.0% oxygen in feed). The cost of phenol production at such conditions was £61.3/ton.
CHAPTER 9

Discussion, Conclusions and Suggestions for Further Work
CHAPTER 6
Discussion, Conclusion, and Suggestions for Further Work

A preliminary investigation into the economics of the direct vapour phase oxidation process for benzene showed that the process could produce phenol at an economically attractive cost, if the possibility of high selectivity (above 60%) for phenol at benzene conversions above 0.7% could be achieved. The conclusion was based on extrapolation of literature data into the low conversion region.

The literature survey indicated that the process conditions suitable for benzene oxidation to phenol are in the region of 600-650°C temperature and 1-2 seconds contact time at atmospheric pressure. Phenol, diphenyl and oxides of carbon were the main products. The process depended on dissociation of the benzene molecule to give a phenyl radical, and phenol formation could take place through the formation of phenoxy radicals.
While diphenyl formation appeared to take place as termination reaction (combination of phenyl radicals), oxides of carbon could form either by surface decomposition of benzene and intermediates, or by degradation of phenol.

Following investigations based on literature data, experimental work was carried out at low conversions of benzene using low concentrations of oxygen and by lowering of the reaction temperature from 630 to 585°C, with and without the use of chloroform as promoter.

The conclusions from the experimental results and treatment of the data were:

1) Lowering of the temperature is the crucial factor in improving the selectivity for phenol.

2) It is difficult to obtain a good selectivity (say, over 50%) with pure benzene feedstock, as dissociation of benzene does not take place at lower temperatures where selectivity could be high. The presence of a promoter helps in lowering the reaction temperature.
3) The promoter plays the major role in the initiation reaction at lower temperatures, while diphenyl formation is the major termination reaction. Chloroform consumption gave a straight line relationship to diphenyl yield.

4) With pure benzene, oxygen did not play any major role in the initiation process, while when chloroform was used, oxygen enhanced the initiation reaction.

5) A part or whole of the combustion reaction takes place through a side reaction, possibly surface reaction.

A final economic optimisation of the process within the limits of the experimental data showed that the optimum conditions (.8% phenol at 69% selectivity) would not present an economically attractive process. However, extrapolation of the experimental data on the basis of semi-empirical relationship gave the following conclusions:

(1) For developing an economically attractive process, investigations should be carried out at a temperature as low as possible, and contact time as high as possible with the use of a promoter.

(2) Extrapolation of the data indicates that the process could be attractive at 565°C temperature and 6 seconds contact time, with .65 mole % of chloroform or similar promoter, the cost of phenol at such conditions being £47.05/ton.

Besides the use of lower temperatures and higher contact times, the following investigations should be carried out for a better understanding of the process:

I) Investigations on the role of surface, using different materials for the reactor and different surface to volume ratio.

II) Investigations at pressures above atmospheric. A pressure range up to 75-100 psi may suppress combustion without any major increase in the cost of equipment.
III) Investigations on the oxidation of phenol in mixture with benzene, to determine the kinetics of its decomposition.
APPENDIX I

TABLE A 1.01

Cost Data for the Evaluation of Phenol Processes

(1) Plant capacity ........... 20,000 tons/year
(2) Capital cost ............. Literature data x cost index correction for 1968 (CPE cost index)
(3) Operating cost .......... Depreciation + interest = 15% of capital cost
Utilities unit cost ........ Utility consumption x unit cost
(4) Unit cost of utilities:
   Electricity ............. £4.5 per $10^3$ KWH
   Steam .................. £1 per ton
   Cooling water .......... £3 per $10^3$ tons
   Fuel .................... £8 per ton
   Labour .................. £1,500 per man year
   Maintenance ) ........... ( 3% of capital cost
   Overheads ) ............. ( 100% of labour + maintenance
(5) Cost of production ...... Depreciation + interest
   + utilities
   + labour
   + maintenance
   + overheads
   + catalysts and chemicals
   + raw material
## TABLE A 1.02

**Cost of Phenol Production by the Direct Vapour Phase Oxidation of Benzene**

<table>
<thead>
<tr>
<th>Yield</th>
<th>Selectivity</th>
<th>Phenol Cost £/ton Air Case</th>
<th>Phenol Cost £/ton Oxygen Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>.4</td>
<td>33</td>
<td>144.5</td>
<td>101.5</td>
</tr>
<tr>
<td>&quot;</td>
<td>50</td>
<td>97.5</td>
<td>86.2</td>
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<td>&quot;</td>
<td>67</td>
<td>87.0</td>
<td>75.8</td>
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<td>&quot;</td>
<td>83</td>
<td>82.4</td>
<td>70.9</td>
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<tr>
<td>&quot;</td>
<td>100</td>
<td>79.8</td>
<td>68.5</td>
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<td>.8</td>
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<td>80.0</td>
</tr>
<tr>
<td>&quot;</td>
<td>50</td>
<td>69.5</td>
<td>63.8</td>
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<tr>
<td>&quot;</td>
<td>67</td>
<td>59.2</td>
<td>53.7</td>
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<tr>
<td>&quot;</td>
<td>83</td>
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<td>&quot;</td>
<td>83</td>
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<td>45.8</td>
<td>45.5</td>
</tr>
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<td>&quot;</td>
<td>67</td>
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<td>35.2</td>
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<tr>
<td>&quot;</td>
<td>83</td>
<td>31.0</td>
<td>30.5</td>
</tr>
<tr>
<td>&quot;</td>
<td>100</td>
<td>28.5</td>
<td>27.0</td>
</tr>
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</table>
### TABLE A2.01

**Literature Data on Yield and Selectivity of Phenol from the Direct Vapour Phase Oxidation of Benzene**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Contact time (sec.)</th>
<th>Oxygen/ Benzene</th>
<th>Yield</th>
<th>Selectivity</th>
<th>Phenol/ Diphenyl</th>
<th>Reference and Comments</th>
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<tr>
<td>600</td>
<td>1</td>
<td>.2</td>
<td>.25</td>
<td>54</td>
<td>5</td>
<td>Lemetre &amp; Caprara (30)</td>
</tr>
<tr>
<td>620</td>
<td>1</td>
<td>.2</td>
<td>.5</td>
<td>33</td>
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</tr>
<tr>
<td>630-640</td>
<td>1</td>
<td>.2</td>
<td>1.3</td>
<td>26</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>660-670</td>
<td>1</td>
<td>.2</td>
<td>1.7</td>
<td>25</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>690-700</td>
<td>1</td>
<td>.2</td>
<td>2.65</td>
<td>22</td>
<td>1.1</td>
<td>Pure benzene feedstock</td>
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<tr>
<td>710-720</td>
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<td>.2</td>
<td>3.4</td>
<td>17</td>
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<tr>
<td>660-670</td>
<td>1</td>
<td>.3</td>
<td>3.1</td>
<td>24</td>
<td>1.4</td>
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<tr>
<td>690-700</td>
<td>1</td>
<td>.3</td>
<td>4.4</td>
<td>23</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>660-670</td>
<td>1</td>
<td>.4</td>
<td>3.5</td>
<td>21</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>690-700</td>
<td>1</td>
<td>.4</td>
<td>4.5</td>
<td>17</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

| 620-630        | 1                   | .2              | 2.2   | 44          | 1.5              | Lemetre & Caprara (30) |
| 630-640        | 1                   | .2              | 2.5   | 40          | 1.5              |                        |
| 640-650        | 1                   | .2              | 2.9   | 36.5        | 1.5              |                        |
| 640-650        | 1                   | .26             | 4.4   | 32          | 1.3              | .5 - 1% ethanolas promoter |
| 650-670        | 1                   | .26             | 5.0   | 34          | 1.3              |                        |
| 640-650        | 1                   | .26             | 4.25  | 32.5        | 1.5              |                        |
TABLE A2.02

Data of Donald and Darlington (70)
on the Effect of Surface/volume ratio

<table>
<thead>
<tr>
<th>Products</th>
<th>Surface/Vol. Ratio = 1.67</th>
<th>Surface/Vol. Ratio = 6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>0.0035</td>
<td>0.007</td>
</tr>
<tr>
<td>Diphenyl</td>
<td>0.0025</td>
<td>0.003</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.0048</td>
<td>0.018</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>0.044</td>
</tr>
</tbody>
</table>
Fig. A3.01

Calibration of the Pyrometer for the Reactor Furnace
Fig. A3.02

Calibration of the Rotameter
Fig. A3.03

Calibration of the Micropump
Flow rate, cc/Min.

Rate of change of level, graduations/sec.

Fig. A3.04

Calibration of the Graduated Level Gauge for Benzene Flow Rate Measurement
Fig. A3.05

Chromatograph Calibration for Phenol and Diphenyl
APPENDIX IV
APPENDIX 4

Set No. 0

**Reactor** - Stainless steel tube, \( \frac{3}{8} \) inch diameter x 22"

**Feed** - Analytical Reagent Grade benzene (0.3 - 0.4% impurities) and air

<table>
<thead>
<tr>
<th>Run No.</th>
<th>001</th>
<th>002</th>
<th>003</th>
<th>004</th>
<th>005</th>
<th>006</th>
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<tbody>
<tr>
<td><strong>Experimental Conditions:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction temperature, °C</td>
<td>350</td>
<td>375</td>
<td>400</td>
<td>455</td>
<td>480</td>
<td>510</td>
</tr>
<tr>
<td>Contact time, seconds</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Oxygen, mole % in feed</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Promoter, mole % on benzene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Products, Moles per 100 Moles of Benzene per Pass:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Diphenyl</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.00</td>
<td>0.05</td>
<td>.21</td>
<td>1.3</td>
<td>1.76</td>
<td>1.95</td>
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<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Water</td>
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<td>-</td>
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<tr>
<td>Hydrochloric acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Benzene conversion</td>
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<td>.008</td>
<td>.035</td>
<td>.216</td>
<td>.293</td>
<td>.325</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Phenol selectivity</td>
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<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
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</table>
### Reactor: Stainless steel

**Feed:** Analytical Reagent Grade benzene (0.3% - 0.4% impurities) and air

<table>
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<tr>
<th>Run No.</th>
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<th>009</th>
<th>010</th>
<th>011</th>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Reaction temperature, °C</td>
<td>530</td>
<td>570</td>
<td>530</td>
<td>505</td>
<td>450</td>
<td>400</td>
</tr>
<tr>
<td>Contact time, seconds</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Oxygen, mole % in feed</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Promoter, mole % on benzene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td><strong>Products, Moles per 100 Moles of Benzene per Pass</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>Trace</td>
<td>Trace</td>
<td>NIl</td>
<td>NIl</td>
<td>NIl</td>
<td>NIl</td>
</tr>
<tr>
<td>Diphenyl</td>
<td>.05</td>
<td>.10</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>2.00</td>
<td>2.10</td>
<td>2.05</td>
<td>2.00</td>
<td>1.70</td>
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<td>Nil</td>
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<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Benzene conversion (%)</td>
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<td>.35</td>
<td>.342</td>
<td>.333</td>
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<td>90.5</td>
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<td>93.0</td>
<td>90.5</td>
<td>77.0</td>
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<td>-</td>
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<tr>
<td>Phenol selectivity (%)</td>
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<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
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Set No. 0
(cont'd)

**Reactor:** Quartz lined

**Feed:** Analytical Reagent Grade benzene (.3 - .5% impurities) and air

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<th>015</th>
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<td>Reaction temperature, °C</td>
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<td>450</td>
<td>500</td>
<td>550</td>
<td>605</td>
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<td>.75</td>
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<td>3.1</td>
<td>3.05</td>
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<td>3.1</td>
</tr>
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<td>Promoter, mole % on benzene</td>
<td>-</td>
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<td>-</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Products, Moles per 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles of Benzene per Pass</td>
</tr>
<tr>
<td>Phenol</td>
</tr>
<tr>
<td>Diphenyl</td>
</tr>
<tr>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
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<tr>
<td>Benzene conversion</td>
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<tr>
<td>Oxygen conversion</td>
</tr>
<tr>
<td>Chloroform consumption</td>
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<td>Phenol selectivity</td>
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Reactor: Quartz lined

Feed: Analytical Reagent Grade benzene (.3 to .5% impurities) and air

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<td>Reaction temperature, °C</td>
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<td>645</td>
<td>620</td>
<td>605</td>
<td>550</td>
<td>505</td>
</tr>
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<td>.75</td>
<td>.75</td>
<td>.75</td>
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<tr>
<td>Oxygen, mole% in feed</td>
<td>3.0</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
</tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td><strong>Products, Moles per 100 Moles of Benzene per Pass</strong></td>
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<td></td>
<td></td>
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<td>Phenol</td>
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<td>.125</td>
<td>.080</td>
<td>.025</td>
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<td>.060</td>
<td>.031</td>
<td>.010</td>
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<td>.75</td>
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<td>.21</td>
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<td>.15</td>
<td>.13</td>
<td>.05</td>
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<td>Water</td>
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<td>-</td>
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<td>.358</td>
<td>.185</td>
<td>.047</td>
<td>.005</td>
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<td>-</td>
<td>-</td>
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<td>Chloroform consumption</td>
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</tr>
<tr>
<td>Phenol selectivity</td>
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</tbody>
</table>
**Set No. 1**

Reactors: Quartz lined

Feed: Pure benzene and air

<table>
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<td>650</td>
<td>650</td>
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<td>650</td>
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<td>.63</td>
<td>.78</td>
<td>1.06</td>
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<td>.5</td>
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<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td><strong>Products, Moles per 100</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moles of Benzene per Pass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
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<td>.086</td>
<td>.122</td>
<td>.160</td>
<td>.074</td>
<td>.111</td>
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<td>.051</td>
<td>.082</td>
<td>.116</td>
<td>.041</td>
<td>.062</td>
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<td>-</td>
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<td>1.42</td>
<td>1.04</td>
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<td>1.00</td>
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<td>1.00</td>
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<td>.731</td>
<td>.477</td>
<td>.621</td>
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<td>70.8</td>
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<tr>
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<td>21.9</td>
<td>15.5</td>
<td>17.9</td>
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</table>
Set No. 1

(Cont'd)

Reactor: Quartz lined

Feed: Pure benzene and air

<table>
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Reactor: Quartz lined

Feed: Pure benzene and air

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**Reactor:** Quartz lined  
**Feed:** Pure benzene and air

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Reactor: Quartz lined
Feed: Pure benzene and air

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**Set No. 2**

**Reactor:** Quartz lined

**Feed:** Pure benzene, chloroform (0.65 mole % on benzene), air

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| Phenol | .484 | .63 | .91 | 1.1 | .73 | .55 |
| Diphenyl | .21 | .33 | .43 | .55 | .49 | .17 |
| Carbon dioxide | .60 | .91 | 1.05 | 1.10 | .91 | .20 |
| Carbon monoxide | .84 | 1.37 | 1.65 | 2.20 | 1.69 | .28 |
| Water | - | - | - | - | - | - |
| Hydrochloric acid | .42 | .645 | .750 | 1.05 | .96 | .37 |

| Benzene conversion | 1.10 | 1.55 | 2.25 | 2.92 | 1.52 | .79 |
| Oxygen conversion |     |     |     |     |     |     |
| Chloroform consumption | .185 | .273 | .348 | .455 | .53 | .17 |
| Phenol selectivity | 44.0 | 40.6 | 40.4 | 32.2 | 48.5 | 68.9 |

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### Set No. 2

**Reactor:** Quartz lined

**Feed:** Pure benzene, chloroform (.65 mole % on benzene) and air

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Reactor: Quartz lined
Feed: Pure benzene, Chloroform and air.

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<td>5.5</td>
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<td>.65</td>
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Reactor: Quartz lined
Feed: Pure benzene, Chloroform and air

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<td>.65</td>
<td>.65</td>
<td>.65</td>
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<td>—</td>
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<td>—</td>
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<td>—</td>
<td>—</td>
<td>—</td>
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<td>—</td>
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<td>Chloroform consumption</td>
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<td>.05</td>
<td>—</td>
<td>—</td>
<td>.10</td>
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<td>Phenol selectivity</td>
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Set No 2 (contd.)

**Reactor:** Quartz lined

**Feed** Pure benzene, Chloroform and air

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<td>Reaction temperature, °C</td>
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<td>585</td>
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<td>610</td>
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<td>7.0</td>
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<td>.65</td>
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<td>.65</td>
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<table>
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<th><strong>Products, Moles per 100 Moles of Benzene per Pass</strong></th>
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<tr>
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<td>.162</td>
<td>.620</td>
<td>.705</td>
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<td>.650</td>
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<td>.490</td>
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<tr>
<td>Hydrochloric acid</td>
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<td></td>
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<td>3.550</td>
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<td>Chloroform consumption</td>
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<td></td>
</tr>
<tr>
<td>Phenol selectivity</td>
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Set No. 3

Reactor: Quartz lined

Feed: Pure benzene or pure benzene with chloroform as promoter

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<td>Reaction temperature, °C</td>
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<td>595</td>
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</tr>
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<td>.78</td>
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<td>Oxygen, mole% in feed</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
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<td>Promoter, mole% on benzene</td>
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<td>.65</td>
<td>.65</td>
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<td><strong>Products, Moles per 100</strong></td>
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<td></td>
</tr>
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<td>Moles of Benzene per Pass</td>
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<td>Phenol</td>
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<td>-</td>
<td>-</td>
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<td>Diphenyl</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
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<td>-</td>
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<td>.16</td>
<td>.074</td>
<td>.246</td>
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<td>-</td>
<td>-</td>
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</tr>
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<td>Promoter</td>
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<tr>
<td>Phenol selectivity</td>
<td>-</td>
<td>-</td>
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</table>
APPENDIX 5

TABLE A5.01

Design Equations and Procedures for the
Economic Optimisation Model

(1) Heat Exchange System

Heat exchanger sizings were calculated on the basis of a simple
programme (89) which evaluates LMTD (Log Mean Temperature Difference)
correction factor \( F_{n-2n} \) for assumed number of shell passes and
iterates to fix the number of passes to get an LMTD correction factor
\( F_{n-2n} \) of .8. This value of LMTD correction factor is accepted as
being near to that of optimum heat exchanger operation in practice.
The set of equations and program flowsheet follows (Table A5.02).

\[
\begin{align*}
T_{51}, T_{52} &= \text{Hot side fluid temperature (inlet = 1, outlet = 2)} \\
T_{C1}, T_{C2} &= \text{Cold side fluid temperature} \\
MTD &= \text{Mean temperature difference} \\
GTD &= \text{Greater temperature difference} \\
LTD &= \text{Lower temperature difference} \\
n &= \text{Number of shell passes} \\
X, R &= \text{Parameters related to the evaluation of LMTD correction factor (90)}
\end{align*}
\]

(2) Furnace (reactor)

The furnace cost was based solely on its heat duty (vide
Table A5.02).

(3) Product Recovery

The Ensko method (90) was used for the calculations for
the distillation columns. 95% recovery of phenol was
assumed. Equilibrium flash calculations were carried
out for the flash separation (90).
(3) Product Recovery

15-20% concentration of phenol was obtained after the flash and the final purity of phenol as product was taken as 93.5%, the rest being diphenyl (1%) and benzene (0.5%). The Gilliland correlation (94) was used to evaluate the number of plates at a reflux ratio taken as 1.5 times the minimum reflux ratio (Fenske method). A plate efficiency of 50% was assumed.

**INPUT**

Temp. conditions, flow rates for different conversions and selectivity for phenol

\[ T_S = T_{S1} - T_{S2} \]
\[ T_C = T_{C2} - T_{C1} \]

Is \( T_S \) or \( T_C = 0 \)

Calculate

\[ T_{S1} - T_{C2} \]
\[ T_{S2} - T_{C1} \]

\( n = 1 \)

Is \( T_{S1} - T_{C2} = T_{S2} - T_{C1} \)

\( R = 1 \)

\( MDT = T_{S1} - T_{C1} \)

Is \( Y = R^2 + 1 \)

Yes

\[ X_{n-2n} = \frac{X}{n-nX + X} \]

\[ Y = \frac{2}{X_{n-2n}} - 1 - R \]

Yes

\[ X_{n-2n} = \frac{1-(1-RX)^n}{(1-RX)^n} \]

\( n = n + 1 \)

No

Yes

Is \( R = 1 \)

No

Yes

Is \( F_{n-2n} = 0.8 \)

\[ F_{n-2n} = \frac{1.414Y}{\ln \frac{Y + \sqrt{R^2 + 1}}{Y - \sqrt{R^2 + 1}}} \]

\[ MTD = \frac{T_S}{2T_D-LTD} \]

\[ R = \frac{T_S}{T_C} \]

\[ MTD_c = MTD \times 0.8 \]

Calculate Area and Cost

---

Table A5.02
Table A5.03

Equipment Costs (91-93)

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Cost Equation</th>
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<tr>
<td>Heat Exchanger</td>
<td>( c = 2.27 (A + 300)^3 )</td>
</tr>
<tr>
<td></td>
<td>where ( A ) = Area ( \text{ft}^2 )</td>
</tr>
<tr>
<td></td>
<td>( c ) = cost, £ (1963)</td>
</tr>
<tr>
<td>Distillation Column</td>
<td>( c = 20.7 \times 1.53 )</td>
</tr>
<tr>
<td></td>
<td>where ( c ) = cost, £/tray (1963)</td>
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<tr>
<td>Furnace</td>
<td>( c = 4800 (X + 2)^1.0 )</td>
</tr>
<tr>
<td></td>
<td>where ( X ) = Heat duty, ( 10^6 ) BTU/Hour</td>
</tr>
<tr>
<td></td>
<td>( c ) = cost, £ (1962)</td>
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<tr>
<td>Pumps</td>
<td>( c = 200 (X + 1)^{.22} )</td>
</tr>
<tr>
<td></td>
<td>( c ) = cost, £ (1960)</td>
</tr>
<tr>
<td></td>
<td>( X ) = ( c ) ft/min. pumping rate</td>
</tr>
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</table>
List of Cost Equations – Process Cost Model

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
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<tr>
<td><strong>WYIELD</strong></td>
<td>Weight % phenol formed per pass</td>
</tr>
<tr>
<td><strong>WSELECT</strong></td>
<td>Weight of phenol produced/weight of benzene consumed</td>
</tr>
<tr>
<td><strong>COSTFUR</strong></td>
<td>Cost of furnace (reactor), £</td>
</tr>
<tr>
<td><strong>COSTVAP</strong></td>
<td>Cost of benzene vapouriser, £</td>
</tr>
<tr>
<td><strong>COSTREC</strong></td>
<td>Cost of phenol recovery system, £</td>
</tr>
<tr>
<td><strong>COSTCOM</strong></td>
<td>Cost of pumps/compression (including motors), £</td>
</tr>
<tr>
<td><strong>COSTCL</strong></td>
<td>Cost of coolers, £</td>
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<tr>
<td><strong>COSTEX</strong></td>
<td>Cost of feed effluent heat exchanger, £</td>
</tr>
<tr>
<td><strong>CAPITAL</strong></td>
<td>Capital cost, £</td>
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<tr>
<td><strong>CFIXED</strong></td>
<td>Fixed charges, £/Hr</td>
</tr>
<tr>
<td><strong>CWATER, CFUEL, CSTM, CPOWER</strong></td>
<td>Utility costs, £/Hr</td>
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<tr>
<td><strong>CBZN</strong></td>
<td>Benzene cost, £/Hr (@ £2.5/ton)</td>
</tr>
<tr>
<td><strong>CPROM</strong></td>
<td>Promoter cost, £/Hr (at benzene price)</td>
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<tr>
<td><strong>CPHEN</strong></td>
<td>Cost of production of phenol, £/ton</td>
</tr>
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<td><strong>TEMP</strong></td>
<td>Reaction temperature, °F</td>
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<tr>
<td><strong>DELT</strong></td>
<td>Design variable (vide Fig. 7.01), BRED = By production credit of fuel value</td>
</tr>
</tbody>
</table>

**Basis** - 20,000 ton/yr of phenol capacity (vide Fig. 7.01)

1) \[ \text{COSTEX} = 5500 + \left( \frac{36 \times 10^5}{\text{DELT}-30} - 5500 \right) \times \frac{1}{\text{WYIELD}} + \frac{120}{\text{WYIELD}} \times (\text{TEMP}-1050) \]

2) \[ \text{COSTFUR} = 7300 + \frac{530}{\text{WYIELD}} \times \text{DELT} \]

3) \[ \text{COSTREC} = 7.0 \left[ \frac{1}{8.35 \times 10^{-2} \text{WYIELD} - 0.0036 \text{WYIELD}^2} - 1 \right]^{0.5} \times 16.8 + 40 \]

4a) \[ \text{COSTVAP (Air Case)} = 2.7 \left( \frac{5250}{\text{WYIELD}} + 300 \right)^{0.9} \times 1.15 \]

4b) \[ \text{COSTVAP (Oxygen Case)} = 2.7 \left( \frac{1350}{\text{WYIELD}} + 300 \right)^{0.9} \times 1.15 \]

5a) \[ \text{COSTCL (Air Case)} = 2.27 \times 1.15 \left( \frac{7500}{\text{WYIELD}} + 300 \right)^{0.9} \]

5b) \[ \text{COSTCL (Oxygen Case)} = 2.27 \times 1.15 \left( \frac{1100}{\text{WYIELD}} + 300 \right)^{0.9} \]

6a) \[ \text{COSTCOM (Air Case)} = 3.5 \times 200 \times \left( \frac{76}{\text{WYIELD}} + 1 \right)^{22} + 7.13 \left( \frac{76}{\text{WYIELD}} + 7.5 \right)^{1.73} \times 1.15 \]

6b) \[ \text{COSTCOM (Oxygen Case)} = 2.2 \times 200 \times \left( \frac{76}{\text{WYIELD}} + 1 \right)^{22} + 7.13 \left( \frac{76}{\text{WYIELD}} + 7.5 \right)^{1.73} \times 1.15 \]

\[ + \left( \frac{21}{\text{WYIELD}} + 10 \right)^{0.79} \times 1000 \]
7) \( \text{CAPITAL} = 4.0 \ (\text{COSTEX} + \text{COSTFUR} + \text{COSTVAP} + \text{COSTREC} + \text{COSTCOM} + \text{COSTCL}) \)

8) \( \text{CWATER} = \frac{0.0155}{\text{WYIELD}} + 0.038 \left( \frac{1}{0.08 \text{WYIELD} - 0.8035 \text{WYIELD}^2} - 1 \right) \)

9) \( \text{CFUEL} = 0.064 \times \frac{\text{DELT}}{\text{WYIELD}} \left( 1 + 0.372 \text{AIRBZN} \right) \)

10) \( \text{CPOWER} = \frac{10}{\text{WYIELD}} \)

11a) \( \text{CSTM} \) (Air Case) = \( \frac{18}{\text{WYIELD}} \)

11b) \( \text{CSTM} \) (Oxygen Case) = \( \frac{3}{\text{WYIELD}} \)

Function to be Minimised

\( \text{CPHEN} = (0.21 \text{CAPITAL}/8000 + \text{CBZN} + \text{CPROM} + \text{CWATER} + \text{CFUEL} + \text{CPOWER} + \text{CSTM}) / 2.5 - \Delta \leq D \)
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Definitions and nomenclature

Volume of the reactor (cc)

\[ \text{Contact time} = \frac{\text{Volume of total feed passing through the reactor per second at the reaction conditions}}{\text{Yield}} \]

\[ \text{Yield} = \frac{\text{Moles of benzene converted to the product}}{\text{Moles of benzene passing through the reactor (single pass)}} \times 100 \]

\[ \text{Conversion} = \frac{\text{Moles of reactant undergoing reaction}}{\text{Moles of reactant passing through the reactor (single pass)}} \times 100 \]

\[ \text{Selectivity} = \frac{\text{Phenol yield}}{\text{Benzene conversion}} \times 100 \]

Promoter consumption = Moles of promoter decomposed per 100 moles of benzene feed.

Phenol/diphenyl ratio = Phenol yield / diphenyl yield.

\( C = \text{Concentration, mole/cc} \)
\( K = \text{Rate constant} \)
\( R^* = \text{Free Radical} \)

A chemical symbol within a bracket indicates concentration in mole/cc, e.g.:

\( (R^*) = \text{Concentration of } R^* \)

\( t = \text{time} \)
\( T = \text{temperature} \)