Catalytic vapour phase oxidation of pseudocumene.

Subir Rao
University of Windsor
CATALYTIC VAPOUR PHASE OXIDATION
OF PSEUDOCUMENE

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by
Subir Rao
B. Tech. (Hons.), Indian Institute of Technology,
Kharagpur, India, 1963

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ABSTRACT

The feasibility of the vapour phase oxidation of pseudocumene was studied qualitatively in a fixed bed reactor. A commercial vanadium pentoxide catalyst containing $10\% V_2O_5$ on inert alumina was used as the catalyst. The air flow rate was kept constant at 30 SCFH corresponding to a contact time of 0.0715 to 0.1 sec. Experiments were conducted for reaction temperatures of 350 to 400°C, catalyst loading of 0.545 to 2.91 cc./gm. mole/hr. and the air to pseudocumene ratios of 17 to 70 by weight. To study the effects of additives on the oxidation process, pseudocumene mixed with heptane, liquid bromine and N-bromo succinimide were fed to the reactor. Trimellitic anhydride dissolved in acetone was also fed to the reactor to ascertain whether it was stable under the reaction conditions employed. Oxidation of o-xylene and durene was carried out to check the suitability of the catalyst and other reaction conditions.

Although o-xylene and durene could be successfully oxidized in the vapour phase to phthalic anhydride and pyromellitic dianhydride respectively, pseudocumene could not be oxidized to trimellitic acid or anhydride for the range of conditions studied. Trace amount of a dicarboxylic acid was obtained in the oxidation products. The complete oxidation of trimellitic anhydride to carbon dioxide indicated that most probably trimellitic anhydride or acid was initially formed as an intermediate in the oxidation process and was later oxidized to carbon dioxide.

These findings agree with those of Morita (20) and Sasayama (21).
ACKNOWLEDGEMENTS

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I. INTRODUCTION

Over the past two decades, the aromatic chemical industry has grown at a very rapid pace. The stimulus for this growth was the demand for strategic raw materials like toluene etc., during the Second World War. The growth has continued till today with the development of plastic and synthetic fibre industry. The volume of total products and the number of derivatives that are assuming commercial importance has increased significantly.

However very little attention has so far been paid to the polymethyl benzenes i.e., benzene derivatives containing two or more methyl substituted groups. Only the first homologue of the group, the three isomers of xylene have been fully explored and their oxidation products, phthalic anhydride, terephthalic acid and isophthalic acid are all commercially important products required in the manufacture of plastics, polyester fibres and resins. Pseudocumene, mesitylene and durene are the next three important higher polymethyl benzenes; the first two among the trimethyl benzenes while the latter among the tetramethyl benzenes. These polymethyl benzenes are now available in commercial quantities and are potential source of raw materials for the growing plasticizer and polyimide resin industries.

These polymethyl benzenes are present in virgin naphtha and petroleum refining streams from the reformer or the catalytic cracker and can be easily and economically separated. Table 1.1 (Appendix I) illustrates the ready availability of the polymethyl benzenes in
different streams of a petroleum refinery.

The aromatics are separated from the petroleum refining streams either by Udex* extraction or by sulfur dioxide Wash oil double extraction process and then fractionated. From the 'C_8' aromatic fraction, o-xylene and ethyl benzene are separated by distillation while the other two isomers para and meta are separated by fractional crystallization. Pseudocumene is separated from the 'C_9' aromatic fraction by distillation. Durene can be separated from the 'C_10' aromatic fraction by crystallization, but the synthesis route via alkylation of pseudocumene or xylenes is a more economical one. Similarly mesitylene is synthesised by isomerization of pseudocumene rather than separating it from the 'C_9' aromatic fraction (2).

At present a very small fraction of the total available aromatics is recovered. No aromatic fractions are recovered from the catalytic cracking stream or virgin naphtha as high olefin content complicates separation. Thus the major portion of the aromatic hydrocarbons is consumed as motor gasoline octane number booster. Certain aromatics are recovered from part of the catalytic reformate stream. Benzene, toluene and the three isomers of xylenes which have captive markets are recovered in larger proportion than the 'C_9' and 'C_10' aromatic fractions. These higher polymethyl benzenes at present find application as solvents for forced dry enamel or insecticide formulations (3). But their ready availability and easier methods of recovery guarantee a potential source of raw materials. At present in the United States, pseudocumene is commerically produced by three refineries (Humble Oil, Hess Oil and Sinclair Petrochemicals), while seven others have potential production

*Universal Oil Products Dow Chemical Extraction process employing a mixture of diethylene - dipropylene glycol and water.
facilities. Similarly two refineries (Humble Oil and Sinclair Petrochemicals) recover durene at present but four more can do so if the market grows bigger (4).

Oxidation of the higher polymethyl benzenes will be a logical answer for their successful utilization. Oxidation of aromatic compounds such as benzene, toluene, o-, m- and p-xylene, and naphthalene are all commercially successful processes providing profitable outlets. Similarly if pseudocumene can be oxidized to trimellitic acid or anhydride, mesitylene to trimesic acid and durene to pyromellitic acid or the corresponding dianhydride, a ready market will be available for the higher polymethyl benzenes. Trimellitic anhydride and pyromellitic dianhydride are used in the manufacture of plasticizers, alkyd resins for water soluble or conventional coatings, high temperature resistant and self lubricating polyester imide, polyamide and polyimide resins, as a curing agent for epoxy resins and as a textile softener and surfactant (5). In fact these anhydrides are better than the conventional anhydride like phthalic anhydride as these contain more number of free acid groups.

These oxidation processes are being slowly developed into full scale commercial plants. AMOCO Chemical Corporation, the only producer of trimellitic anhydride in the world, has successfully developed the "Mid century" liquid phase air oxidation process for pseudocumene and at present is building up a 50 million lbs. per year plant in Joliet, Illinois (6). DuPont produces pyromellitic dianhydride for captive use by a liquid phase nitric acid oxidation process from durene. Hexagon Laboratory also has a similar liquid phase oxidation process (7).
Princeton Research Laboratory and Ruhröl Chemie Werk in Germany have successfully developed the vapour phase air oxidation processes for durene, which are very similar to the o-xylene oxidation process (8).

But at present these acid anhydrides are produced on a very small scale. The total production of trimellitic anhydride is less than 10 million lbs. per year, while that of pyromellitic dianhydride is around 2 million lbs. per year (9). The main reason for this small market is the higher price of these compounds in comparison to the conventional plasticizers. One solution will be large scale production, which will lead to large scale recovery of pseudocumene and durene. This will, in turn, lower the cost of the raw materials which constitute about 70 to 80% of the total cost. However, the success depends more on perfection of the existing processes to achieve higher conversion and efficiency.

The oxidation of pseudocumene requires special attention from this aspect. At present it is only carried out in the liquid phase. The vapour phase process, which has many advantages over the liquid phase process will be an ideal alternative route. Some of the advantages are outlined below:

1. The vapour phase oxidation processes are generally continuous, fully automatic and requires minimum number of operating personnel.

2. The vapour phase processes employ large capacity reactors, reducing the initial plant cost.

3. In the vapour phase processes, temperatures above the dew point of steam are maintained in the reactors and condensers which reduces the corrosion problems. On the other hand, high pressure combined with bromine containing catalysts warrant use of special materials of construction and alloys for the liquid phase processes.
4. Unlike the liquid phase process, the catalyst and the liquid media from the reaction products need not be separated in the vapour phase processes.

5. In the vapour phase oxidation, impure raw materials can be used, as the impurities in the feedstock are generally burnt away during the reaction and the purity of the end products is not affected.

6. The vapour phase oxidation process is easily adaptable to the fluidized reactor technique which leads to better control, higher yields and larger capacity plants.

So far both o-xylene and durene having at least a pair of methyl groups in the ortho position have been successfully oxidized to the corresponding anhydrides in the vapour phase.

\[ \text{o-Xylene} + 6 \text{O} \xrightarrow{V_{2}O_{5}} \text{Phthalic anhydride} + 3 \text{H}_{2}\text{O} \quad (1.1) \]

\[ \text{Durene} + 12 \text{O} \xrightarrow{V_{2}O_{5}} \text{Pyromellitic dianhydride} + 6 \text{H}_{2}\text{O} \quad (1.2) \]
Pseudocumene also contains a pair of methyl groups in the ortho position and it is therefore logical to expect that it can also be oxidized in the vapour phase, either to trimellitic anhydride or 4-methyl phthalic anhydride.

The scope of the present work is to investigate the feasibility of the catalytic vapour phase oxidation of pseudocumene using the conventional vanadium pentoxide catalyst and air as the oxidizing agent.
II. LITERATURE SURVEY

Although the oxidation of many aromatic hydrocarbons into carboxylic acids has been studied extensively, very little attention has so far been paid to the oxidation of higher polymethyl benzenes and particularly to pseudocumene. A brief review of the investigations done on the oxidation of pseudocumene both in the liquid and vapour phases and that of o-xylene and durene in the vapour phase is presented below. A short review on the analytical techniques used to analyse the expected oxidation products is also included.

A. Liquid Phase Oxidation of Pseudocumene

The oxidation of pseudocumene by chromic oxide in glacial acetic acid or potassium permanganate and sodium hydroxide to trimellitic acid has been reported in the Beilstein (10) and is one of the earliest works in this line. Recently, pseudocumene has been oxidized to trimellitic acid in the liquid phase by 30% nitric acid in the presence of HCl, HBr, and alkali metal chloride or bromide like NH₄Cl or NH₄Br (11, 12, 13). A yield of 89.5% with an acid product containing 7.9% nitration impurities was obtained. The yield and purity of the product depended on the acid concentration and the reaction temperature, pressure and duration. To reduce the nitric acid consumption, certain Russian scientists (14, 15) carried out this reaction in two stages, first with air or a mixture of air and oxygen in the ratio of 1:1 and thence with nitric acid. Yields up to 96 to 97% were obtained. Cobalt stearate was used as the catalyst for the air oxidation step.
The present commercial oxidation process for pseudocumene to trimellitic acid is known as the Mid Century process and is a generalized liquid phase air oxidation process for polymethyl benzenes (16, 17). It uses a heavy metal such as cobalt, manganese or molybdenum and a form of bromine as the catalyst. These metals are usually used in the form of salts which are soluble in the liquid phase under the reaction conditions. Naphthenates and acetates are usually used. Bromine which provides a regenerable source of chain initiating free radicals is introduced as a free element or as a compound such as benzyl bromide, ammonium bromide, potassium bromate or acetylene tetrabromide. Since many of the acid products are solid at the reaction temperature, a liquid which is stable under the reaction conditions is used as a transport medium. This liquid medium also provides efficient contact between air and the hydrocarbon. The liquid medium should be therefore chosen in such a way that it should dissolve the hydrocarbon and the catalyst but not necessarily the acid products. Acetic acid is an ideal solvent for this purpose. The reaction conditions are more or less similar for different hydrocarbons. A temperature between 125°C and 275°C is usually maintained. Pressures up to a maximum of 40 atmospheres are required to maintain the liquid phase. It also assists in increasing the partial pressure of oxygen in the system. The reaction time for most of the alkyl aromatics is half an hour to three hours. Air is generally used as the oxidizing agent and an excess oxygen of 5 to 15% is enough for complete conversion.

The above oxidation process can be carried out batchwise, semicontinuously or continuously. In a typical batch operation, the required amount of the hydrocarbon, the solvent and the catalyst are...
charged to the reactor. The reactor is next heated to the initiation
temperature and air is bubbled through the reaction mixture after
pressurizing to the required pressure. The heat of reaction is removed
either by condensing and refluxing the solvent vapours or by circulating
cooling water in coils. When the oxygen content of the evolved gas
indicates completion of reaction, the reactor is depressurized and the
solid acid products are separated from the solvent and the catalyst by
centrifuging. The centrifuge cake is washed to remove the adhering
solvent and dried. The filtrate is distilled to remove the water formed
during the reaction and the solvent is then recycled. The residue from
the above distillation contains the catalyst components and the partially
oxidized products. A 80 to 90% conversion of the hydrocarbon to the
aromatic carboxylic acid is obtained. The high temperature and the
bromine containing acidic system warrant the use of special stainless
steels and alloy steels for the construction of the reactor and
auxiliary equipment. The exact operating conditions for the oxidation of
pseudocumene are not, however, available.

Shipman (18) studied the feasibility of the liquid phase oxidation
of pseudocumene and other polymethyl benzenes using sulfur dioxide as
the oxidizing agent, with and without any catalyst. Batch reactors of
100 cc., 1 litre and 25 litres were used. The experimental procedure
consisted of charging the reactor with a known quantity of the hydrocarbon,
assembling it into the furnace in a blastproof reactor bay, heating to
the reaction temperature and pressurizing with sulfur dioxide. As the
reaction proceeded, the pressure dropped due to the consumption of sulfur
dioxide and additional amount was added intermittently to maintain the reaction pressure. At the end of the reaction, the products were removed from the reactor either by blowing up through a dip pipe at around 200°C or by cooling the reactor and dismantling it.

Shipman's experimental findings were as follows:

1. In the presence of excess sulfur dioxide, the oxidation of pseudocumene proceeded stoichiometrically according to the following reaction:

\[ R-CH_3 + 1-1/2 \text{SO}_2 \rightarrow R-COOH + 1-1/2 \text{S} + \text{H}_2\text{O} \]  

2. The reaction appeared to be homogeneous and was not affected by any catalyst.

3. The activation energy of the oxidation of pseudocumene, xylene and toluene were \( 42 \pm 2 \text{ Kcal./mole} \).

4. The overall reaction rate was approximately proportional to the square of the hydrocarbon concentration and approximately to the 1.8th power in case of pseudocumene.

5. The reaction rate decreased with increasing pressure, even after correcting the rate with respect to the change in concentration of the hydrocarbon.

6. Neither the reaction rate nor the product quality varied with the purity of the hydrocarbon feed.

7. The reaction was not affected by the presence of oxygen or air (5 atm. of oxygen in a total pressure of 300 atm.) or free radical initiators and inhibitors, metal salts, metal oxides and chlorine compounds.
8. The reaction was catalysed by bromine, iodine or their compounds. In case of pseudocumene, presence of 1% hydrobromic acid lowered the activation energy to 21 Kcal./mole and the increase in the rate was proportional to the logarithm of the hydrobromic acid concentration. Most probably, bromine atom abstracted a hydrogen atom from a substituted methyl group, thus lowering the activation energy of the overall reaction.

9. The reaction was completely inhibited by the presence of metallic silver or copper.

10. The quality of the product did not improve by introducing a solvent such as acetic acid or water. On the other hand, the corrosion became severe.

11. The yield of the carboxylic acids decreased as the number of methyl substituted groups increased (Table 1.2 in Appendix I).

12. The yield also depended on the average reaction rate per unit volume of the reactor. For the oxidation of pseudocumene the following yields were obtained:

<table>
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<tr>
<td>(i) $&lt; 10 \times 10^{-6} \text{ gr. mole/ml.}$</td>
<td>$&gt; 80%$</td>
</tr>
<tr>
<td>(ii) $&gt; 30 \times 10^{-6} \text{ gr. mole/ml.}$</td>
<td>$50%$</td>
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13. The major byproduct in the oxidation of pseudocumene was 4-methyl phthalic anhydride.

B. Vapour Phase Oxidation of Pseudocumene

In comparison to the liquid phase process, very few attempts to oxidise pseudocumene in the vapour phase have been reported in the
literature. Ibing (19) in the 7th World Petroleum Congress in Mexico reported that several tests were conducted in the Ruhröl Chemie Werk, West Germany to study the feasibility of the catalytic vapour phase oxidation of pseudocumene. Yields of 35 to 40% by weight of trimellitic anhydride were obtained. 4-methyl phthalic anhydride and maleic anhydride were the two main byproducts. There was also disproportion reaction leading to the formation of considerable amounts of pyromellitic dianhydride and phthalic anhydride. Isolation and separation of trimellitic anhydride from the reaction products were very difficult and expensive.

Morita (20), while studying the vapour phase oxidation of methyl naphthalenes, also studied the oxidation of 1, 2, 4 and 1, 2, 3 trimethyl benzenes using a $\text{V}_2\text{O}_5$-$\text{Mo}_3$ pumice stone catalyst. An air rate of 150 litres/hour, the hydrocarbon feed rate of 1.5 grams/hour, the catalyst volume of 50 cc. and the reaction temperature of 400°C were used. Phthalic anhydride and benzoic acid were obtained in case of o-xylene and toluene respectively. But both 1, 2, 3 and 1, 2, 4 trimethyl benzenes formed maleic anhydride (3% yield) and carbon dioxide, accompanied by very small amounts of the corresponding benzene tricarboxylic acids. No phthalic anhydride or benzoic acid was obtained. Furthermore, the oxidation of 1, 2, 4 benzene tricarboxylic acid gave no phthalic anhydride but only maleic anhydride (5% yield) and carbon dioxide. No unreacted material was found in any of the oxidation reactions. The yields of maleic anhydride obtained in the oxidation of 1, 2, 4 benzene tricarboxylic acid and 1, 2, 4 trimethyl benzene are comparable; therefore benzene
tricarboxylic acid was presumably formed as an intermediate. However, decarboxylation of the extra carbonyl group did not ensue and the benzene ring was cleaved to form maleic anhydride and carbon dioxide.

\[
\begin{align*}
\text{CH}_3 & \quad \text{COOH} \\
(0) & \quad \text{O} + \text{CO}_2
\end{align*}
\]

Pseudocumene \quad \text{Trimellitic acid} \quad \text{Maleic anhydride}

Sasayama (21), from his studies of the vapour phase oxidation of the alkyl aromatic hydrocarbons, concluded that:

1. The side chains of an alkyl benzene are oxidized to the \(-\text{COOH}\) group one by one.

2. On further heating, the benzene carboxylic acid formed loses the \(-\text{COOH}\) group one by one and is reduced to benzene.

3. Benzene on further oxidation is converted to maleic anhydride.

The following mechanism will represent the oxidation of a trimethyl benzene:

\[
\begin{align*}
\text{CH}_3 & \quad \text{COOH} \\
+ & \quad 0
\end{align*}
\]

1, 3, 5 Trimethyl Benzene (Mesitylene)
Sasayama further reported that the major controlling factors for the oxidation reaction were the catalyst, the reaction temperature and the air to hydrocarbon ratio. The oxidation was most sensitive to the hydrocarbon to air ratio.

C. Vapour Phase Oxidation of o-Xylene and Durene

O-Xylene and durene, both of which contain a pair of methyl groups in the ortho position have been successfully oxidized in the vapour phase and these processes are now-a-days followed in commercial plants. Exhaustive work has been done on the oxidation of o-xylene (22, 23).

In the commercial oxidation of o-xylene (24, 25), either employing a fixed bed or a fluidized bed reactor, o-xylene is vaporized and mixed with preheated air in the ratio of 1:30 to 40 by weight. The fixed bed reactor is a shell and tube heat exchanger, with the tubes filled with 10% vanadium pentoxide on inert alumina as the catalyst. Molten salt is

[Diagrams and chemical reactions are shown here, illustrating the oxidation process and chemical structures.]
circulated on the shell side to remove the heat of reaction and maintain isothermal condition. A reaction temperature of 900 to 1000°F and a contact time of 0.1 to 0.15 sec. gives an overall yield of 70-80%. The reaction gases containing phthalic anhydride, carbon dioxide, water vapours and partially oxidized hydrocarbons such as maleic anhydride and benzoic acid are cooled in a heat exchanger and condensed in an air cooled condenser. Crude phthalic anhydride is distilled to obtain a product of 99.5% purity.

The vapour phase oxidation of durene is very similar to that of o-xylene. Miller (26, 27) successfully oxidized durene using air in the ratio of 30 to 200 by weight. The catalyst was vanadium oxide on a carrier of relatively low surface area to volume ratio such as silicon carbide or alumina. A temperature of 850 to 1000°F was used. The reaction products contained pyromellitic dianhydride, carbon dioxide, water vapours and minor amounts of ring rupture derivatives. The reactor consisted of a three feet long tube of 5/8 in. inside diameter, jacketted with a mercury bath and charged with 50 to 100 cc. of the catalyst. An air rate of 40 to 70 moles per hour and a durene feed rate of 0.05 to 0.3 moles per hour were used. Yields of 80 to 102.5 weight percent of pyromellitic dianhydride of 92 to 96% purity were obtained. The amount of catalyst did not affect the yield significantly. A higher reaction temperature of 890°F instead of 850°F increased the yield but the purity of the product was reduced. The hydrocarbon to air ratio had a significant effect on the overall yield of the reaction. Addition of a wet scrubber to the condenser resulted in the recovery of about 5 weight percent of anhydride as free acid.
Beach (28) also has reported a successful vapour phase air oxidation of durene under similar reaction conditions. The catalyst contained 10% vanadium pentoxide on corundum and promoted with 0.1% of potassium sulfate. Catalysts containing molybdenum oxide and promoters such as various salts were also tried. Mostly a reaction temperature of 450°C, a feed containing 0.05 to 0.1 mole percent of durene and a contact time of 0.1 to 1 second were used. The main product recovered was the tetracarboxylic acid because, most probably, the dianhydride formed initially was later hydrolyzed to the acid by the water formed during the reaction.

D. Analytical Techniques

From the above literature survey, the reaction products from the oxidation of pseudocumene should contain the following compounds or a mixture of them:

1. Trimellitic anhydride
2. Trimellitic acid
3. 4-methyl phthalic anhydride
4. Maleic anhydride
5. Phthalic anhydride
6. Pyromellitic dianhydride
7. Carbon dioxide and water vapours
8. Unreacted pseudocumene.

Either trimellitic anhydride or trimellitic acid was the main constituent of the oxidation products of pseudocumene in the liquid phase oxidation processes. Shipman (18) and Ibing (19) reported the presence of 4-methyl phthalic anhydride in the reaction products. Ibing (19), Morita (20) and Sasayama (21) reported the presence of maleic anhydride. Ibing also
reported the formation of phthalic anhydride and pyromellitic dianhydride. A brief review of the analytical techniques used to analyse the above compounds or their mixtures is presented below.

In the literature, no analytical method for analysing trimellitic anhydride has been reported so far. Schnitzer and Desjardins (29) analysed different benzene carboxylic acids including trimellitic acid by gas chromatography using a 4 ft. x 1/4 in. outside diameter copper tube, packed with 10% SE-30 on 80-100 mesh Chromosorb W HMDS treated. But acids were converted into their methyl esters and injected into the column dissolved in acetone. The mono- and dicarboxylic acids were methylated with methanol in presence of few drops of sulfuric acid. The tricarboxylic and higher acids were methylated with diazomethane generated from Diazald.

Berman et al. (30) have reported the ultraviolet absorption spectra for all the twelve benzene carboxylic acids including trimellitic acid. The trimellitic acid was dissolved in distilled water and analysed in a Beckman Model DU spectrophotometer using a 1 cm. cell. Trimellitic acid showed a significant absorption peak at a wave length of 275 nu.

Nicholson (31) has reported the quantitative analysis of mono- and polybasic benzene carboxylic acids in potassium bromide discs by infrared spectrophotometry. Methyl terephthalic acid, 4-methyl isophthalic acid and 4-methyl phthalic acids were analysed using a Perkin Elmer Model 21 spectrophotometer. With mixing time of 60 secs., reproducibility of 6% could be obtained. With higher and lower mixing times, average deviations as large as 50% were obtained. Wide fluctuations, 30 to 50% in the intensities of infrared absorption for certain methyl substituted
isophthalic acids, were noted in 10 to 15% of the discs tested. However, plots of absorptivity of the benzene carboxylic acids against the concentration of the acids in the pellets were essentially linear. 4-methyl phthalic acid showed absorption peak at a wave length of 12.55 microns.

Paetkau (23) analysed the oxidation products of o-xylene by gas chromatography using a 6 ft. x 1/4 in. outside diameter, stainless steel column packed with Chromosorb W 60/80 mesh and coated with 25% Dow Corning Silicone Oil plus 2% phosphoric acid. The column temperature was maintained at 252°C and helium gas was used as the carrier gas. The analysis was carried out with a Beckman GC-2A gaschromatograph, equipped with a thermal conductivity detector. The condensate from the condenser and the uncondensed gases were analysed separately. The condensate was dissolved in acetone before injecting it into the chromatograph. Very good separation for o-xylene, o-tolualdehyde, o-toluic acid, maleic anhydride, phthalic anhydride and phthalide were obtained. Although the column deteriorated with time, no difference with the working of the thermal conductivity detector was observed because of the reaction with phosphoric acid bleeding from the column. Phosphoric acid is necessary to prevent tailing and it has been recommended by certain gaschromatograph manufacturers to use gold plated detectors to reduce corrosion due to the bleeding of phosphoric acid from the column (32).

Various references are available in literature, suggesting ultraviolet and infrared spectrophotometry to detect pseudocumene or other alkyl benzenes. However, a convenient method will be one using a gaschromatograph. A recent trade catalog (33) has reported very good separation of
pseudocumene from other alkyl aromatics and non-hydrocarbons on a 6 ft. x 3/16 in. 2% Carbowax 20M on Porasil C column at a column temperature of 100°C.
III. EXPERIMENTAL SET UP AND PROCEDURE

The vapour phase catalytic oxidation of pseudocumene was studied in a differential reactor using vanadium pentoxide on inert alumina as the catalyst and air as the oxidizing agent. The oxidation products were identified by determining the melting points and neutralization equivalents of the compounds and confirmed by running their infrared spectrums. The details of the flow system and the individual equipment are given below. The specifications of all other equipment are given in Appendix IV.

A. Flow Diagram

The experimental equipment consisted of an air preheater, a reactor, a carburetor, pseudocumene feeding system, condensers, and a number of temperature, pressure and flow measuring devices. A schematic diagram of the experimental set up is given in Figure 1. High pressure air at 90-95 psig., tapped from the laboratory compressed air line, was reduced to the required pressure range of 0-10 psig. by means of a low pressure regulator (PR1). A stone air filter was installed in the line to remove any dirt, oil or water accompanying the compressed air. The air flow rate was controlled by means of a fine needle control valve (NV1) and measured by means of a rotometer (R1) of 0-60 SCFH air capacity. The air was preheated to 350-400°C in an electrically heated air preheater packed with 1/4 in. berl saddles and mixed with the pseudocumene vapours in the carburetor. Pseudocumene was fed to the carburetor from a feed tank by nitrogen displacement. Its flow rate was controlled by means of a fine needle valve (NV2) and measured by a rotometer (R2) of 0-22 cc./min. capacity. The
FIG. 1 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SET UP
carburetor, packed with 1/4 in. berl saddles and heated electrically, provided a thorough mixing of the pseudocumene vapours and the air and also heated the mixture to the reaction temperature. The reactant mixture next entered the differential reactor. The reactor was heated electrically and had three distinct zones:

1. Preheating zone
2. Reaction zone
3. Product heating zone

Both the preheating and the product heating zones are packed with 1/4 in. berl saddles while the reaction zone contained the catalyst bed. In the preheating zone, the temperature of the reactant mixture was brought to the desired temperature of 400-450°C. Since the reaction was highly exothermic, once the reaction started, the heat to the reaction and product heating sections were reduced to maintain isothermal condition across the catalyst bed. The oxidation products were condensed in a series of condensers with either air or water as the coolant. The temperature was measured at six different locations of the system by means of chromel-alumel thermocouples. These points have been indicated as TC on the flow diagram. Pressure was also measured just before the air rotameter and at the inlet and outlet of the reactor.

B. Details of Equipment

1. Reactor

The details of the reactor are shown in Figure 2. It was made from a 1 1/4 in. long and 1-1/2 in. I.D., schedule 40, 304 stainless steel pipe. The ends of the pipe were welded to 300 psig welding neck flanges and closed with matching blind flanges. Aluminum gaskets of 1/8 in. thickness
FIG. 2 SECTIONAL VIEW OF THE REACTOR.
FIG. 3 SECTIONAL VIEW OF THE PREHEATER.
were used to make leakproof joints. Two 1/8 in. dia. thermowell tubes extending right up to the catalyst bed were welded to the end flanges to insert the 1/16 in. dia. thermocouples. Two 3/8 in. dia. stainless steel tubes were also welded to the end flanges to insert the berl saddles into the reactor.

The differential reactor bed consisted of a 5-1/2 in. long and 1-3/8 in. O.D. stainless steel cartridge. The ends of the cartridge were closed with stainless steel screens, which fitted snugly to the reactor tube. The cartridge was filled with a mixture of the catalyst and 1/4 in. berl saddles to minimize nonuniformity of the bed and channelling effects. The cartridge was placed in the centre of the reactor and the rest of the space was filled with 1/4 in. berl saddles.

The reactor was heated electrically by three independently controlled heating sections of 3-1/2 in., 5 in. and 3-1/2 in. lengths and rated at 700, 1160, 700 watts at 110v. To control the temperature in each zone, the voltage applied to each heating unit was varied by means of variable transformers. The reactor unit was completely insulated with glass wool insulation supplied by Johns Manville.

2. Air Preheater

A sectional view of the air preheater is shown in Figure 3. The construction was basically identical to that of the reactor except that it was longer by 4 in. than the reactor tube. It was completely packed with 1/4 in. berl saddles and was heated by means of two 12 in. long semicircular heating units, each of 700 watts at 110v, connected in parallel. Two 1/8 in. dia. thermowells were welded to the top and bottom blind flanges for inserting the thermocouples.
FIG. 4  SECTIONAL VIEW OF THE CARBURETOR.

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3. **Carburetor**

The carburetor (Figure 4) was made from a 11 in. long and 2 in. nominal dia., schedule 40 pipe. The bottom end was closed completely by welding a 3 in. dia. x 1/2 in. thick plate, while the top end was welded to a 2 in. dia. standard pipe flange and closed with a matching blind flange, with 1/8 in. thick copper gasket. The pseudocumene liquid from the feed tank was sprayed into the air stream from the preheater by means of five 1/16 in. dia. holes drilled into the inlet tubing. The carburetor was packed with 1/4 in. berl saddles. The carburetor was heated by two 8 in. long semicircular heating units, each of 500 watts at 110v. and connected in parallel. Power input to the heater was controlled by means of a variable transformer. The carburetor was also insulated with glass wool insulation supplied by Johns Manville.

4. **Pseudocumene Feeding System**

Pseudocumene was fed to the carburetor from a mild steel feed tank, made from a 15 in. long and 5 in. nominal diameter, schedule 40 pipe. The bottom end was completely closed by welding to a 6 in. dia. x 1 in. thick plate while the top end was welded to a 5 in. diameter standard flange and closed with a matching blind flange with a neoprene rubber gasket. Three 1/4 in. brass male connectors were tapped to the top blind flange for connecting the nitrogen feed line, pseudocumene discharge line and the air purge line to the feed tank. The 1/4 in. copper pseudocumene discharge line extended to within 1/2 in. of the tank bottom. A 1/2 in. swagelok male connector with a plug end was also provided on the top of the feed tank for feeding pseudocumene. Pseudocumene from the discharge line was fed to the carburetor through two stainless steel needle valves, the
pseudocumene rotameter and a check valve.

C. **Analytical Method**

In the absence of a suitable and convenient analytical technique, all efforts were concentrated to find out the presence of anhydrides and carboxylic acids in the reactor effluents. Since all anhydrides (maleic, phthalic, trimellitic, 1-methyl phthalic and pyromellitic) and acids (trimellitic) are solids at room temperature while pseudocumene is a liquid, deposition of a solid in the all glass condenser tube was a clear indication of the presence of desired products in the reactor effluent. Whenever any solid was deposited, its melting point and neutralization equivalent were determined. Later the products were purified by dissolving in acetone and decolourizing with activated carbon and recrystallizing by addition of a suitable solvent (mostly n-heptane). The melting points and neutralization equivalents of the purified samples were determined to confirm the initial identification. This identification was further confirmed by running the infrared spectrum of the sample and comparing it with that of the expected compounds. All infrared spectra were run on a Beckman IR-10 model infrared spectrophotometer.

D. **Catalyst**

In the vapour phase oxidation of o-xylene to phthalic anhydride and durene to pyromellitic dianhydride a vanadium pentoxide catalyst, supported on an inert carrier with low surface area have been used. A similar catalyst was used for the vapour phase oxidation of pseudocumene. The catalyst was of commercial grade vanadia oxidation catalyst supported on inert alumina and was supplied by M/S Harshaw Chemical Co., Cleveland, Ohio, U.S.A. The physical properties of the catalyst are given in Table I.3 in Appendix I.
E. **Selection of Raw Materials**

Pseudocumene used in the experiment was commercial grade supplied by M/S Hess Oil and Chemical Corporation from their Corpus Christi, Texas refinery. It was of 95% purity and the analysis is given in Table I.4, Appendix I.

-o-Xylene and durene used in certain trial runs were of Eastman Kodak practical grade of 95% purity supplied by M/S Fisher Scientific Co.

-Trimellitic anhydride, trimellitic acid, 4-methyl phthalic anhydride and pyromellitic dianhydride used for calibration purposes were of Eastman Kodak practical grade supplied by M/S Fisher Scientific Co.

-Phthalic anhydride and maleic anhydride used for calibration purposes were of Fisher certified grade supplied by M/S Fisher Scientific Co.

-Potassium bromide used to make pellets for the infrared spectrophotometry was of I.R. grade, supplied by M/S Harshaw Chemical Co., Cleveland, U.S.A.

F. **Calibration Procedure**

1. **Calibration of the Air Rotameter**

The rotameter to measure the flow rate of air was calibrated by measuring the actual flow rate of air by means of a precision wet test gas meter. Since air is practically insoluble in water, the presaturator of the wet test meter was filled with distilled water. The upstream pressure and temperature of the air were measured by a pressure gauge and a thermocouple installed in the lines before the rotameter. The calibration curve is given in Figure 5 in Appendix II. This calibration curve has been drawn by converting the flow rates at different inlet pressures to equivalent flow rates at an hypothetical inlet pressure of.
Thus the same calibration curve was used for finding out the flow rates for different inlet pressure conditions after multiplying by the corresponding correction factors.

2. **Calibration of the Pseudocumene Rotameter**

The rotameter to measure the flow rate of pseudocumene was calibrated by collecting pseudocumene for a fixed time in a burette. Since the effect of small pressure and temperature difference on liquid is negligible, the calibration curve at room temperature and pressure was used for the complete experimental range. The calibration curve is given in Figure 6 of Appendix II.

3. **Calibration of Thermocouples**

Chromel-alumel ungrounded type thermocouples were used to measure the temperature of the inlet and outlet of the catalyst bed. Since the reactor, the preheater and the carburetor all were heated electrically by A.C., an induced e.m.f. (up to 2 mv.) used to accumulate in the system in spite of grounding. This led to erroneous measurement of temperatures. The above ungrounded type thermocouples were selected to eliminate this error due to induced e.m.f. The rest of the four thermocouples were of ungrounded type and were used for approximate temperature indication purposes only.

All the thermocouples were calibrated against the melting point of ice and chemically pure tin metal. The observed temperatures were extremely close to the literature values.

G. **Experimental Procedure**

The heaters for the preheater, the reactor and the carburetor were switched on and different variable transformers were adjusted to heat the...
system slowly to the desired temperature. Before switching on the heaters, the air supply valve was opened and air was fed continuously. The air flow rate was measured by the rotameter and controlled by the fine needle control valve at the outlet of the rotameter. After the desired temperature was reached, pseudocumene was fed to the carburetor by pressurizing the feed tank with nitrogen to 16 psig. The flow rate of pseudocumene was controlled by the needle valve just at the inlet to the pseudocumene rotameter. The fluctuations in the flow rate were stabilized by adjusting the second needle control valve just at the outlet of the pseudocumene feed tank. Once the reaction started, the heat supply to the reaction and product heating zone of the reactor was reduced to maintain the desired isothermal temperature of the differential catalyst bed.

After feeding pseudocumene for about 15 minutes, the condensers were connected to the reactor exit tube. Most of the runs were conducted for about an hour. After this the liquid sample was collected from the condenser and solid deposited in the condenser tube was removed for product identification. In certain trials, the exhaust from the condenser tube was injected into a gas chromatograph with a silica gel followed by a molecular sieve column to check the presence of carbon dioxide.

For overnight shutdown, the heat supply to the experimental set up was cut off but the air flow was continued till all the equipment was cooled to the room temperature. The nitrogen supply to the pseudocumene was cut off and the feed tank was depressurized. If the feed tank was left pressurized overnight, slugs of vapour appeared from time to time in the pseudocumene rotameter and interfered with its flow rate measurement.
These slugs were due to the dissolved nitrogen coming out of solution as the pressure in the pseudocumene feed line to the carburetor decreased after the flow through the needle control valves. Whenever the catalyst in the reactor was changed, it was pressure tested for 10 psig, after recharging the reactor. All the lines connecting different equipment were insulated with electric heating tapes to avoid condensation of water vapours or any solid products.
IV. RESULTS AND DISCUSSION

Following the procedure outlined in Chapter III experimental runs were made for the following range of reaction conditions:

1. Reaction temperatures of 350°C, 400°C and 450°C.
2. Catalyst amounts of 15 gms., 41.7 gms. and 80 gms.
3. Air to pseudocumene ratios of 17.5, 40 and 67.5 by weight.
4. Feed containing pseudocumene alone or mixed with heptane, bromine and N-bromo succinimide.

The air flow rate was kept constant at around 30 SCFH. This corresponded to a contact time of 0.0715 sec. for the cartridge containing only 1/4 in. catalyst spheres and 0.1 sec. for the cartridge containing 1/4 in. berl saddles for gas flow rates at 400°C. Since the vapour phase oxidation of pseudocumene appeared to be very similar to that of o-xylene and durene, o-xylene and durene dissolved in heptane were also fed to the reactor to confirm whether the reaction conditions are in the right range. Finally to ascertain whether trimellitic anhydride was formed initially and later was oxidized to carbon dioxide, pure trimellitic anhydride dissolved in acetone was also fed to the reactor. A summary of observations of different experimental runs are given below under the following headings:

1. Effect of temperature.
2. Effect of air to pseudocumene ratio.
3. Effect of catalyst loading.
4. Effect of additives.
5. Oxidation of o-xylene
6. Oxidation of durene
7. Oxidation of trimellitic anhydride.

A. Effect of Temperature

Experimental runs for three different reaction temperatures of 350°C, 400°C and 450°C were conducted varying the air to pseudocumene ratios and keeping the catalyst amount constant (Table 1.5 in Appendix I). In all the runs no solid deposit was observed in the condenser tube except for a negligible quantity of dirty crust in certain cases. The condensate collected from the condenser was a liquid having two distinct layers; a pale yellow top layer of about 80-90% of the total volume and a bottom layer of dark yellow to brown colour. At 450°C the colour of the bottom layer was darker, while at a higher air to pseudocumene ratio and a lower temperature, the colour of the top layer was lighter. At 350°C there was only one layer having a density very close to that of pseudocumene. This indicated that the oxidation reaction was not taking place at a lower temperature of 350°C. This is in agreement with the findings of Miller (26), who while studying the vapour phase oxidation of durene reported that oxidation did not ensue below a temperature of 370°C. Vanadium pentoxide’s function as a catalyst depends on its ability to freely interchange its valences and below a temperature of 370°C vanadium oxide is incapable of being reoxidized from its lower to higher valence states by the use of air alone.

The top layer in other cases also had densities very close to that of pseudocumene. The bottom dark layer was most probably due to the
formation of tarry materials due to the rupture of the benzene ring. A higher temperature was favourable for these side reactions to proceed. From these observations further experiments were carried out at 400°C.

B. **Effect of Air to Pseudocumene Ratio**

Experiments at three different air to pseudocumene ratios of 17.5, 40 and 67.5 by weight were conducted (Table I.5 in Appendix I). No effect was observed on the oxidation reaction. No solid deposit was observed in the condenser. The colour of the liquid condensate collected from the condensers was lighter at higher air to pseudocumene ratios. The major noticeable difference was in the condition of the exhaust from the condenser. There was a white smoggy exhaust from the condenser in all the trials for a condenser exit temperature of 10 to 15°C. The exhaust did not improve even after incorporation of a liquid nitrogen trap. This exhaust was relatively free of condensable vapours at a higher air to pseudocumene ratio than at the lower ones. This may be due to the formation of an eutectic mixture of unreacted pseudocumene and air in the reactor effluent which needs a very low temperature for complete condensation.

These findings are contrary to those of Sasayama (21) who reported that the vapour phase oxidation of alkyl benzenes was very sensitive to the air to hydrocarbon ratio.

C. **Catalyst Loading**

Experiments with three different weights of catalyst 15 gms., 41.7 gms. and 80 gms. were carried out (Table I.5 in Appendix I). These
corresponded to catalyst loadings of 0.547, 7.52 and 2.91 eq./gm. -
moles/hr. A reaction temperature of 400°C and an air to pseudocumene ratio
of 67.5 by weight were used for the first catalyst loading. No solid
deposit was observed in the condenser tube. The condensate was of
single layer and light colour having a density and refractive index
very close to that of pseudocumene. Few samples were injected to a
gas chromatograph and even at the highest attenuation no peak was
observed for carbon dioxide. This indicated that the oxidation did not
proceed at this low catalyst loading.

For the second case different temperatures and air to pseudocumene
ratios were tried. Although there was no deposition of solid in the
condenser tube ample indications that pseudocumene was oxidized to carbon
dioxide was obtained. When the exhaust was bubbled through alcoholic
sodium hydroxide solution, a white precipitate was obtained which completely
dissolved in hydrochloric acid. This precipitate may be sodium carbonate
otherwise, sodium salt of any benzene carboxylic acid would have left the
solid benzene carboxylic acid when dissolved in hydrochloric acid.

In two experimental runs the condenser tube was washed with acetone
and when evaporated a small amount of solid product was obtained.
Infrared spectrums of these samples were run (Figure 14 and 15 in
Appendix III). Strong absorption in the far infrared range indicates
the compound to be an acid. Strong absorption bands at wave lengths of
1700, 1420, 1250 and 910 CM⁻¹ confirm that the sample is an acid. Absence
of bands at wave lengths of 1500 and 1600 CM⁻¹ indicates that the acid is
most probably a straight chained dicarboxylic acid. The spectrum has no
resemblance at all with that of other expected oxidation products of
pseudocumene such as, trimellitic anhydride, trimellitic acid, maleic anhydride and \( H \)-methyl phthalic anhydride (Figures 7, 8, 11 and 12 in Appendix III). In fact the characteristic bands of an anhydride group at wave lengths of 1850 and 1780 \( \text{cm}^{-1} \) are completely absent. Since a very small amount of the sample was obtained, the neutralization equivalent of the sample could not be determined to facilitate identification.

In case of the third catalyst loading for a reaction temperature of \( 400^\circ\text{C} \) and an air to pseudocumene ratio of 67.5 by weight, no solid deposit was obtained in the condenser tube as in the previous two cases. The liquid condensate contained a dark brown bottom layer. The sample could not be decolourized even after 5 to 6 times repeated treatment with activated carbon after dissolving in acetone. No solid residue was left, when a part of this partly decolourized sample was completely evaporated. Infrared spectrums of the bottom layer between two \( \text{KBr} \) pellets were run but no useful information could be obtained as the water present in the sample fogged the \( \text{KBr} \) pellets completely. The density of this bottom layer was 1.1445 gms./cc. and may be certain tarry materials formed due to the rupture of the benzene ring. The top light coloured layer had a density of 0.8816, and may be unreacted pseudocumene. When certain samples of the exhaust of the condenser were injected into a gas chromatograph, peaks were observed for carbon dioxide, oxygen and nitrogen indicating that complete oxidation of pseudocumene was taking place.

The catalyst loadings used in the present investigation were within the values reported in the literature. Morita (20) in the vapour phase
oxidation of pseudocumene used a catalyst loading of 7.35 cc./gm. moles/hr. Miller (26) used two different catalyst loadings of 0.772 and 1.5 cc./gm. moles/hr. in the vapour phase oxidation of durene but did not observe any difference in the yield of the final product.

D. Effective of Additives

1. Heptane

Since there was no arrangement of feeding a solid into the reactor, durene was dissolved in heptane and a 20.8% solution was fed to the reactor. Durene was successfully oxidized to pyromellitic acid in the vapour phase and it was thought that heptane might be responsible for this success. Therefore a 20% solution of pseudocumene in heptane was fed to the reactor. A temperature of 400°C, a catalyst loading of 2.9 cc./gm. moles/hr. and an air to pseudocumene ratio of 348 by weight were used. The exhaust from the condenser was clear but no liquid condensate was collected from the condenser. The condenser tubes were cleaned with acetone and the resulting solution was decolourized by repeated treatment with activated carbon. When this decolourized solution was evaporated, no solid was deposited but a small crust of tarry material was left behind. This indicated that addition of heptane had no effect on the success of the oxidation of durene and simply acted as a transport medium.

2. Bromine

In the liquid phase oxidation of pseudocumene by air in the Mid-century process (16, 17) and by sulfur dioxide (18) a form of bromine is used as a catalyst. Therefore pseudocumene mixed with about 0.1% of bromine liquid was fed to the reactor. As in the previous case a reaction
temperature of 400°C and a catalyst loading of 2.9 cc./gm. moles/hr. were used. An air to pseudocumene ratio of 69.5 by weight was maintained. The exhaust from the condenser was not completely free from condensable vapours. A dark coloured liquid sample was collected. Part of this condensate and the condenser wash liquid was decolourized by repeated treatment with activated carbon and recrystalized after boiling to saturation by adding heptane. No solid separated out. A dirty white paste like material of negligible amount was left at the bottom of the beaker. This indicated that addition of bromine had no effect on the oxidation process.

3. **N-Bromo-Succinimide**

To further ascertain the effect of bromine, 0.2 to 0.3 gms. of N-bromo succinimide which releases Br⁺ ions was dissolved in 5 cc. of benzene and added to one liter of pseudocumene. The same reaction conditions as in the previous trial were maintained. The exhaust from the condenser was not completely free of condensable vapours. A dark liquid condensate was obtained from the condenser as in the previous cases. But when this liquid and the condenser wash liquid were decolourized and recrystalized about 0.15 gms. of a solid white precipitate was obtained. The solid had a melting point of 186°C and a neutralization equivalent of 75.8. The melting points of pure trimellitic anhydride and trimellitic acid are 165 to 168°C and 229°C respectively and the corresponding theoretical neutralization equivalents are 64.0₄ and 70.0₄. Therefore no conclusions could be drawn as to the composition of the solid based on its melting point and neutralization equivalent. An infrared spectrum of the sample
(Figure 16 in Appendix I) was run. The spectrum is exactly same as that of the oxidation products of pseudocumene alone. The position of different bands are exactly at the same wave lengths. Only the peak heights are different. From the infrared spectrum the compound may be identified to be a dicarboxylic acid as in the previous case.

E. Oxidation of o-Xylene

Since o-xylene is also a liquid it was fed to the feed tank directly and pumped to the reactor at the same rate as pseudocumene. The same oxidation conditions as pseudocumene, a reaction temperature of 400°C, an air to o-xylene ratio of 67 to 70 by weight for two different catalyst amounts of 15 gms. and 80 gms. were used. In all the trials beautiful crystals dirty white to brownish in colour separated out in the condenser tube. In case of low catalyst loading a pale yellow liquid having density and refractive index very close to that of o-xylene was collected from the condenser. There was no condensate in the latter case. This liquid was most probably due to the unreacted o-xylene in the reactor effluent stream. The higher catalyst loading in the latter case may be responsible for complete oxidation without leaving any unreacted hydrocarbon. The solid separated in the condenser tube had a melting point of 105°C and a neutralization equivalent of 90. The solid was dissolved in acetone, decolourized by repeated treatment with activated carbon and recrystallized by boiling to saturation and adding heptane. The yellowish white precipitate obtained was filtered and dried. It had a melting point of 170°C and a neutralization equivalent of 85.3. The melting points of pure phthalic anhydride and phthalic acid are 129 to 131°C and 206 to
208°C, respectively, while their theoretical neutralization equivalent are 74.06 and 83.06. From this it may be concluded that the solid sample obtained is a mixture of phthalic anhydride and phthalic acid. Although the vapour phase oxidation should result in the formation of phthalic anhydride, phthalic anhydride might have reacted with water vapours formed during the reaction and converted to phthalic acid.

The infrared spectrum of an impure solid sample (Figure 17 in Appendix III) was run and compared with that of pure phthalic anhydride (Figure 9 in Appendix III). The positions of different bands are more or less at the same wave lengths. However, the peaks are much smaller, which can be attributed to the presence of impurities in the sample. The characteristic bands of the anhydride groups, are at wave numbers of 1850, 1750, 1240 and 885 CM⁻¹ against 1850, 1760, 1255 and 900 CM⁻¹ of the pure compound. From this analysis it may be concluded that the sample is phthalic anhydride.

However, the infrared spectrum of the recrystallized sample (Figure 18 in Appendix III) indicated the compound to be an acid. Strong absorption in the far infrared region is a clear indication of presence of an acid. The other characteristic band of acid is also present at a wave number of 1675 CM⁻¹. The characteristic band of anhydride group at a wave number of 1850 CM⁻¹ is prominent but the other one at a wave number of 1770 CM⁻¹ is very much depressed. The bands at wave numbers of 1580 CM⁻¹ and 1490 CM⁻¹ may be attributed to the presence of a benzene ring. From this analysis it can be concluded that the sample is most probably a mixture of phthalic acid and phthalic anhydride.
These experimental runs confirmed that o-xylene could be successfully oxidized in the vapour phase under conditions for which pseudocumene could not be oxidized.

F. Oxidation of Durene

Since durene was a solid at room temperature and there was no arrangement of feeding a solid directly into the reactor, durene was dissolved in heptane and a 20.8% solution was fed to the reactor. Similar reaction conditions which were used in case of o-xylene and pseudocumene were used. A reaction temperature of 400°C and a catalyst loading of 2.9 cc./gm. moles/hr. were maintained. The air flow rate was kept unchanged at 30 SCFH which increased the air to durene ratio to 217 by weight. There was no liquid condensate from the condenser. The exhaust of the condenser was completely free from condensable vapours. An interesting phenomena was observed. When water was used as the coolant in the first condenser the colour of the solid deposit in the condenser was bright yellow which turned dirty brown when left open to the atmosphere overnight. When air was used as the coolant the bright yellow colour did not appear and a dirty brown deposit was obtained right from the beginning. The solid deposit was washed with carbon tetrachloride to remove any unreacted durene, filtered and dried. The melting point and neutralization equivalent of the solid deposits were 262-265°C and 60 in case of air cooling and 225°C and 73.2 in one run and 220°C and 81.2 in another run with water cooling. Besides, the amount of solid collected was more in quantity and dirtier in colour in the latter cases. The last sample was dissolved in acetone, decolourized by repeated treatment.
with activated carbon and recrystallized by boiling to saturation and adding heptane. The purified sample had a melting point of $225^\circ C$ and a neutralization equivalent of 73.00. The bright yellow colour was most probably due to the presence of certain free radicals and cooling with water was responsible for the presence of low boiling impurities. The melting points and neutralization equivalent of pure pyromellitic acid and pyromellitic dianhydride are 286 to 288°C, 257 to 265°C (decomp.) and 54.53 and 63.51 respectively. From this analysis it may be concluded that the solid sample obtained under air cooling is either pyromellitic dianhydride or pyromellitic acid mixed with impurities.

To further ascertain the identification, the infrared spectra of two samples (Figures 19, 20 in Appendix III) were run and then compared with that of the pure pyromellitic dianhydride (Figure 10 in Appendix III). All the significant bands matched exactly with those of the pure compound. This confirms that the sample obtained is pyromellitic dianhydride. It is thus proved that durene can be oxidized successfully in the vapour phase to pyromellitic dianhydride under the reaction conditions for which pseudocumene could not be oxidized.

G. Oxidation of Trimellitic Anhydride

To ascertain whether trimellitic anhydride was initially formed as an intermediate in the oxidation of pseudocumene and was later further oxidized to carbon dioxide, trimellitic anhydride dissolved in acetone (in 20% solution) was fed to the reactor. Same reaction conditions which were used in case of pseudocumene, o-xylene and durene were used. A reaction temperature of 400°C and a catalyst loading of 2.9 cc./gm. moles/hr. were used. The air to trimellitic anhydride ratio of 55.8 by
weight was maintained. The exhaust from the condenser was free of condensable vapours and a light yellow liquid of density 1.0145 gm./cc was collected as the condensate. This liquid seemed to be water formed during the oxidation reaction. No solid deposit of any kind was obtained. This confirms that the trimellitic anhydride is unstable at the reaction conditions of the vapour phase oxidation and is most probably oxidized further to carbon dioxide. These findings agree with those of Morita (20) and Sasayama (21). Morita from the vapour phase oxidation of pseudocumene and the corresponding benzene tricarboxylic acid concluded that most probably the trimellitic acid was formed as an intermediate in the oxidation process and was later further oxidized to maleic anhydride and carbon dioxide. It is thus confirmed that pseudocumene can not be oxidized to trimellitic acid or anhydride in the vapour phase for the range of reaction conditions studied.
V. CONCLUSIONS AND RECOMMENDATIONS

Pseudocumene could not be oxidized to trimellitic acid or anhydride in the vapour phase for the range of reaction conditions studied. On the other hand, o-xylene and durene were successfully oxidized in the vapour phase to phthalic anhydride and pyromellitic dianhydride respectively, under the reaction conditions identical to those employed for the oxidation of pseudocumene. Furthermore under similar reaction conditions trimellitic anhydride was completely oxidized to carbon dioxide. Most probably trimellitic anhydride or acid was initially formed as an intermediate in the oxidation of pseudocumene and was later oxidized to carbon dioxide.

To further ascertain the feasibility of the vapour phase oxidation of pseudocumene, investigations should be carried out for a wider range of reaction conditions. The recommendations outlined below may be useful guidelines for future investigations:

1. A suitable quantitative analytical technique preferably using a gas chromatograph should be perfected to analyse all the possible constituents of the reactor effluents. Chromatographic techniques used by Paetkau (23) and Mann et al. (34) will provide useful guidelines. The solid and liquid products in the reactor effluent should be separated in suitable traps and injected into the chromatograph dissolved in acetone. The non-condensible gases can be directly injected into the gas chromatograph through a gas sampling valve.
2. Experiments using catalysts containing molybdenum oxide and promoters such as potassium sulphate besides vanadium pentoxide should be conducted.

3. Experiments under milder oxidation conditions, may be, using air mixed with ammonia or sulfur dioxide should also be carried out.

4. Since, most probably, the free acid group present in the trimellitic anhydride is responsible for the rupture of the ring, it will be worthwhile to investigate the vapour phase oxidation of 3,4-dimethyl benzoic acid and its methyl ester.
REFERENCES


12. ibid, 60:4062c, (1964).

13. ibid, 57:4602a, (1962).


15. ibid, 62:11742d, (1965).


32. Wilkens Instrument and Research, Walnut Creek, California, Aerograph Research Notes, Fall issue, pp. 3, (1961).


APPENDIX I

Tables I.1 to I.5
Table I.1 (1)  
Aromatics from a 1000 barrels/day Refinery in the Gulf Coast of U.S.A.  
(in 1000 tons)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Aromatic Compounds</th>
<th>Virgin Naphtha</th>
<th>Catalytically Cracked Naphtha</th>
<th>Catalytically Reformed Naphtha</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Benzene</td>
<td>25</td>
<td>15</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>2.</td>
<td>Toluene</td>
<td>85</td>
<td>280</td>
<td>80</td>
<td>445</td>
</tr>
<tr>
<td>3.</td>
<td>'C₈' aromatics:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>a. Ethyl benzene: 21.2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>b. p-Xylene: 18.3%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c. o-Xylene: 20.1%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>d. m-Xylene: 40.4%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>'C₉' aromatics:</td>
<td>115</td>
<td>145</td>
<td>155</td>
<td>415</td>
</tr>
<tr>
<td></td>
<td>a. Pseudocumene: 41.3%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>b. Mesitylene: 7.6%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>'C₁₀' aromatics:</td>
<td>115</td>
<td>90</td>
<td>110</td>
<td>315</td>
</tr>
<tr>
<td></td>
<td>a. Durene: 8.3%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Table I.2  
Yields of Carboxylic Acids from  
Alkyl Aromatics

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Toluene</td>
<td>Benzoic acid</td>
<td>300</td>
<td>300</td>
<td>3</td>
<td>&gt; 90%</td>
</tr>
<tr>
<td>2.</td>
<td>p-Xylene</td>
<td>Terephthalic acid</td>
<td>280</td>
<td>300</td>
<td>6</td>
<td>90%</td>
</tr>
<tr>
<td>3.</td>
<td>Pseudocumene</td>
<td>Trimellitic acid</td>
<td>270</td>
<td>300</td>
<td>8</td>
<td>80%</td>
</tr>
<tr>
<td>4.</td>
<td>Durene</td>
<td>Pyromellitic acid</td>
<td>250</td>
<td>300</td>
<td>-</td>
<td>very low</td>
</tr>
</tbody>
</table>

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Table I.3
Physical Properties of the Catalyst

1. Type: Vanadia Oxidation Catalyst
   V-0501 S 1/4 in.

2. $V_2O_5$ Content: 10%

3. Apparent bulk density: 80 lbs./cu. ft.

4. Surface area: 1.0 sq. m./gm.

5. Size: 1/4 in. spheres
Table I

Analysis of Pseudocumene

1. A.P.I. gravity @ 60°F (A.S.T.M. - D 287): 29.4
2. Specific gravity @ 60: .8796
3. Freezing Point °F: -47
4. Flash Point (A.S.T.M. TCC) °F: 121
5. Explosive Limits:
   Upper: 6.0
   Lower: 1.0
6. Refractive Index @ 20°C: 1.5045
7. Colour (A.S.T.M. - D 156): +30
8. Doctor Test: sweet
9. Corrosion (A.S.T.M. - D 130): pass
10. Corrosion (full distillation): pass
11. Neutrality of residue: neutral
12. Distillation (A.S.T.M.)
   I.B.P.: 336
   5%: 337
   10%: 337
   20%: 337
   30%: 337
   40%: 337
   50%: 337
   60%: 337
   70%: 337
   80%: 337
   90%: 337
   95%: 337
13. Dry End Point: 338
14. Distillation Recovery: 98.5%
15. Distillation Residue: 1.0%
16. Distillation Loss: 0.5%
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Catalyst gms.</th>
<th>Temp. °C</th>
<th>Air to H.C. Ratio</th>
<th>Solid Deposition</th>
<th>Liquid Condensate</th>
<th>Exhaust from Condenser</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>15.0</td>
<td>400</td>
<td>40:1</td>
<td>No solid deposit.</td>
<td>Liquid practically of one layer, dark yellow in colour, having a density of 0.9 gms./cc. and refractive index 1.517.</td>
<td>The exhaust from the condenser was not free of condensable vapours for an exit temp. of 52°F. No carbon dioxide peak detected in the gaschromatograph.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>67.5:1</td>
<td>No solid deposit.</td>
<td>Same as above. The colour was lighter. Density 0.885 to 0.9 gms./cc and R.I. 1.5 to 1.51.</td>
<td>Same as above.</td>
</tr>
<tr>
<td>2.</td>
<td>42.7</td>
<td>400</td>
<td>40:1</td>
<td>No solid deposit.</td>
<td>Liquid contained two layers: 10% dark bottom layer and 90% pale yellow top layer.</td>
<td>The exhaust from the condenser was not free of condensable vapours.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.5:1</td>
<td>No solid deposit.</td>
<td>Liquid condensate of practically one layer, very light yellow and of density of 0.876 gms./cc.</td>
<td>Same as above.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>450</td>
<td>No solid deposit.</td>
<td>Yellow bottom layer and 90% pale yellow top layer.</td>
<td>Same as above. When exhaust was bubbled through alcoholic NaOH, a white ppt. which dissolved completely in HCl was obtained.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>38:1</td>
<td>No solid deposit.</td>
<td>Practically of one layer, dark yellow of 0.9 gms./cc. density.</td>
<td>- Do -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>350</td>
<td>No solid deposit.</td>
<td>Liquid had two layers, 90% top layer of light yellow colour and 10% bottom dark layer.</td>
<td>- Do -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>38.4:1</td>
<td>- Do -</td>
<td>- Do -</td>
<td>- Do -</td>
</tr>
<tr>
<td>3.</td>
<td>80.0</td>
<td>400</td>
<td>67.5:1</td>
<td>- Do -</td>
<td>Liquid had two layers, top layer of 0.886 gms./cc. density and bottom thick suspension of 1.155 gms./cc.</td>
<td>Exhaust was not free of condensable vapours. Carbon dioxide peaks were obtained in gaschromatograph.</td>
</tr>
</tbody>
</table>
APPENDIX II

Calibration Curves for the Rotameters

Figures 5 and 6
FIG. 5 Calibration Curve for the Air Rotameter
FIG. 6 CALIBRATION CURVE FOR THE PSEUDOCUMENE ROTAMETER
APPENDIX III

Infrared Spectrums

Figures 7 to 20
FIG. 7 INFRARED SPECTRUM OF TRIMELLITIC ANHYDRIDE.

FIG. 8 INFRARED SPECTRUM OF TRIMELLITIC ACID.

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FIG. 9 INFRARED SPECTRUM OF PHTHALIC ANHYDRIDE.

FIG. 10 INFRARED SPECTRUM OF PYROMELLITIC DIANHYDRIDE.
FIG. 11 INFRARED SPECTRUM OF MALEIC ANHYDRIDE.

FIG. 12 INFRARED SPECTRUM OF 4-METHYL PHTHALIC ANHYDRIDE.
FIG. 13 INFRARED SPECTRUM OF PSEUDOCUMENE.

FIG. 14 INFRARED SPECTRUM OF OXIDATION PRODUCT OF PSEUDOCUMENE (SAMPLE NO: 1).

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FIG. 15 INFRARED SPECTRUM OF OXIDATION PRODUCT OF PSEUDOCUMENE (SAMPLE NO: 2).

FIG. 16 INFRARED SPECTRUM OF OXIDATION PRODUCTS OF PSEUDOCUMENE MIXED WITH N-BROMO-SUCCINIMIDE.

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FIG. 17 INFRARED SPECTRUM OF OXIDATION PRODUCTS OF O-XYLENE (IMPURE SAMPLE).

FIG. 18 INFRARED SPECTRUM OF OXIDATION PRODUCTS OF O-XYLENE (RECRYSTALLIZED SAMPLE).
FIG. 19 INFRARED SPECTRUM OF OXIDATION PRODUCTS OF DURENE (SAMPLE NO: 1).

FIG. 20 INFRARED SPECTRUM OF OXIDATION PRODUCTS OF DURENE (SAMPLE NO: 2).

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APPENDIX IV
EQUIPMENT SPECIFICATIONS

1. Air Filter
Make: Trerice & Co.
Type: Model No. 40
Capacity: 275 CFM at 80-100 lbs. air (max)
Maximum pressure: 300 psig.
Filter screen: stone

2. Low Pressure Regulator (PR 1 in Figure 1)
Make: Matheson of Canada Ltd.
Type: Model No. 70A
Inlet pressure: up to 250 psig.
Outlet pressure: 0-10 psig.
Inlet hose connection: Matheson reinforced butyl rubber hose to withstand 2500 psig.

3. Air Rotameter (0-60 SCFH) (R1 in Figure 1)
Make: Schutte & Koerting Co.
Type: 'Safeguard' rotameter, Series 18000
Meter size: 2-R
Tube no: 2-Rb
Float no: R-21, stainless steel
Scale: 250 mm.
Capacity: 1.05 CFM air at 70°F and 14.7 psia.
4. **Air Rotamer (0-300 SCFH)**

Make: Schutte & Koerting Co.

Type: 'Safeguard' rotameter, series 1800 with 'HCF' high capacity fluted tube

Meter size: 3

Tube no: 3-HCF b

Float no: 34-J stainless steel

Scale: 250 mm.

Capacity: 5-46 CFM air at 70°F and 14.7 psia

5. **Air Control Valve (NV 1 in Figure 1)**

Make: Matheson Canada Ltd.

Type: Instrument type metering valve (model no. 940-B)

Body: Brass

Packing: Buna-N

6. **Check Valves (CV 1 and CV 2 in Figure 1)**

Make: Matheson Canada Ltd.

Capacity: 100 SCFH air at 10 psig. inlet pressure

Max. pressure: up to 2000 psig.

Cracking pressure: approx. 1 psig.

<table>
<thead>
<tr>
<th>Duty</th>
<th>Model</th>
<th>Material of Construction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>400-X</td>
<td>Brass, Neoprene o-ring, stainless steel spring</td>
</tr>
<tr>
<td>Pseudocumene</td>
<td>401-X</td>
<td>Stainless steel 303, viton o-ring, stainless steel spring</td>
</tr>
</tbody>
</table>
7. **Pseudocumene Rotameter (R2 in Figure 1)**

Make: Matheson Canada Ltd.

Type: Dual float rotameter

Tube no: 602

Flow capacity: 0-6.6 cc./min. with 'pyrex' float and 0-24 cc./min. with stainless steel float

8. **Selector Switch**

Type: Thermovolt multipolar rotary switch - UPMF 16/2 (16 point selection)

9. **Electric Heating Units**

Make: 'lindberg'

Type: Heavy duty semi cylindrical units for 1000°C

<table>
<thead>
<tr>
<th>Duty</th>
<th>Model</th>
<th>Diameter inch</th>
<th>Length inch</th>
<th>Watts (two pieces at 115v)</th>
<th>Connection</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Preheater</td>
<td>50231</td>
<td>2-3/8</td>
<td>12</td>
<td>1400</td>
<td>parallel</td>
</tr>
<tr>
<td>2. Carburetor</td>
<td>50221</td>
<td>2-3/8</td>
<td>8</td>
<td>1000</td>
<td>parallel</td>
</tr>
<tr>
<td>3. Reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. top</td>
<td>50301</td>
<td>3</td>
<td>3-1/2</td>
<td>600</td>
<td>series</td>
</tr>
<tr>
<td>b. middle</td>
<td>50311</td>
<td>3</td>
<td>5</td>
<td>850</td>
<td>parallel</td>
</tr>
<tr>
<td>c. bottom</td>
<td>50301</td>
<td>3</td>
<td>3-1/2</td>
<td>600</td>
<td>series</td>
</tr>
</tbody>
</table>
10. **Variable Transformers**

<table>
<thead>
<tr>
<th>Duty</th>
<th>Make</th>
<th>Type</th>
<th>Amps.</th>
<th>Requirement at 115 volt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Preheater</td>
<td>General radio</td>
<td>W50MBB</td>
<td>40</td>
<td>12.2</td>
</tr>
<tr>
<td>2. Carburetor</td>
<td>Powerstat</td>
<td>116B</td>
<td>10</td>
<td>8.7</td>
</tr>
<tr>
<td>3. Reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. top</td>
<td>Powerstat</td>
<td>116</td>
<td>8</td>
<td>5.2</td>
</tr>
<tr>
<td>b. middle</td>
<td>Powerstat</td>
<td>116B</td>
<td>10</td>
<td>7.4</td>
</tr>
<tr>
<td>c. bottom</td>
<td>Powerstat</td>
<td>116</td>
<td>8</td>
<td>5.2</td>
</tr>
<tr>
<td>4. Heating tapes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Preheater to</td>
<td>Powerstat</td>
<td>116</td>
<td>8</td>
<td>3.5</td>
</tr>
<tr>
<td>carburetor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Carburetor to</td>
<td>General Radio</td>
<td>W5MT</td>
<td>5</td>
<td>1.00</td>
</tr>
<tr>
<td>reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c. Reactor to</td>
<td>General Radio</td>
<td>W5MT</td>
<td>5</td>
<td>1.00</td>
</tr>
<tr>
<td>condenser</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

11. **Thermocouples (Catalyst bed inlet and outlet)**

Make: Thermocouple products

Type: Chromel-alumel, series \( \frac{1}{4} \)1/16" O.D.

Junction: \( W_4 \) ungrounded.

The rest of the thermocouples are of chromel-alumel but of \( W_2 \) grounded junction type. These thermocouples do not show the true temperature due to interference of induced e.m.f. of 1 mv to 2 mv in the apparatus set up because of heating with A.C. coils but were used for rough indication purposes.
VITA AUCTORIS

1942 Born in Cuttack, India on January 2.

1963 Received the Bachelor of Technology (Hons.) degree in Chemical Engineering from the Indian Institute of Technology, Kharagpur, India.

1963-66 Worked as Assistant Chemical Engineer in the Technical Department of DCM Chemical Works, New Delhi, India.

1966 Accepted into the Graduate School of the University of Windsor, Windsor, Ontario as a candidate for the degree of Master of Applied Science in Chemical Engineering.