Catalytic vapour phase ammoxidation of pseudocumene.

Michael D. Preudhomme

University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation
https://scholar.uwindsor.ca/etd/6873

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000ext. 3208.
CATALYTIC VAPOUR PHASE AMMOXIDATION
OF PSEUDOCUMENE

A Thesis
Submitted to the Faculty of Graduate Studies Through the Department of Chemical Engineering in Partial Fulfilment of the Requirements for the Degree of Master of Applied Science at the University of Windsor

by

Michael D. Preudhomme
B. A. Sc., University of Windsor, Windsor, Ontario

Windsor, Ontario
March, 1970
INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.
ABSTRACT

The vapour phase air oxidation of pseudocumene over a 50 gram sample of commercial vanadium pentoxide catalyst containing 10% $V_2O_5$ on inert alumina was studied. The air flow rate was kept constant at 30 SCFH corresponding to a contact time of 0.2 seconds while reaction temperatures of 350 to 450°C were studied. Maleic anhydride, carbon dioxide and water were obtained as products.

The vapour phase ammoxidation of pseudocumene over a commercial vanadium pentoxide catalyst and over a 20% $MoO_3$ on inert alumina catalyst was studied. The air flow rate was kept constant at 30 SCFH and molar ratios of pseudocumene to oxygen to ammonia of 1:5:15; 1:5:20; and 1:5:25, corresponding to contact times of 0.11 to 0.16 seconds were maintained. Temperatures were varied from 350 to 450°C. The products were maleic imide, carbon dioxide and water.

The ammoxidation of o-xylene was carried out under identical reaction conditions to the pseudocumene ammoxidation and the products obtained were o-tolunitrile, phthalonitrile and benzonitrile.
Although the air oxidation and ammoxidation of pseudocumene resulted in the rupture of the benzene ring for the range of conditions studied, the ammoxidation of o-xylene was carried out successfully without cleavage of the benzene ring.

A 20% solution of trimellitic anhydride in acetone was oxidized by air oxidation and by ammoxidation over a commercial vanadium pentoxide catalyst and at temperatures of 400 to 450°C. The trimellitic anhydride was completely oxidized to carbon dioxide and water.
ACKNOWLEDGEMENTS

The author wishes to take this opportunity to express his gratitude to his advisor, Dr. G.P. Mathur, for his constructive criticisms, and invaluable guidance and to Dr. M. Adelman for suggestions on numerous occasions.

The author is also grateful to Mr. Geo. Ryan for his technical assistance, Mr. R. Morettin for aid in conducting the literature survey, and Mrs. P.A. Preudhomme for typing the thesis.

M/S Harshaw Co., U.S.A., and Aldrich Chem. Co. supplied, free of cost, the catalysts used in this programme. The financial support for the work was provided by the National Research Council of Canada.
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td></td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. LITERATURE SURVEY</td>
<td>10</td>
</tr>
<tr>
<td>A. Liquid Phase Oxidation of Pseudocumene</td>
<td>10</td>
</tr>
<tr>
<td>B. Vapour Phase Oxidation of Pseudocumene</td>
<td>13</td>
</tr>
<tr>
<td>C. Vapour Phase Oxidation of o-Xylene</td>
<td>14</td>
</tr>
<tr>
<td>D. Vapour Phase Oxidation of Durene</td>
<td>15</td>
</tr>
<tr>
<td>E. Ammoxidation of o-Xylene</td>
<td>15</td>
</tr>
<tr>
<td>III. EXPERIMENTAL EQUIPMENT</td>
<td>17</td>
</tr>
<tr>
<td>A. Flow Diagram</td>
<td>17</td>
</tr>
<tr>
<td>B. Details of Equipment</td>
<td>21</td>
</tr>
<tr>
<td>1. Reactor</td>
<td>21</td>
</tr>
<tr>
<td>2. Air Preheater</td>
<td>23</td>
</tr>
<tr>
<td>3. Carburetor</td>
<td>25</td>
</tr>
<tr>
<td>4. Pseudocumene Feeding System</td>
<td>27</td>
</tr>
<tr>
<td>C. Catalyst</td>
<td>27</td>
</tr>
<tr>
<td>D. Raw Materials</td>
<td>29</td>
</tr>
<tr>
<td>E. Analytical Equipment</td>
<td>30</td>
</tr>
<tr>
<td>1. Air Oxidation of Pseudocumene</td>
<td>30</td>
</tr>
<tr>
<td>2. Ammoxidation of Pseudocumene</td>
<td>31</td>
</tr>
<tr>
<td>IV. EXPERIMENTAL PROCEDURE</td>
<td>32</td>
</tr>
<tr>
<td>A. Calibration Procedure</td>
<td>32</td>
</tr>
<tr>
<td>1. Calibration of the Air Rotameter</td>
<td>32</td>
</tr>
<tr>
<td>2. Calibration of the Ammonia Rotameter</td>
<td>32</td>
</tr>
<tr>
<td>3. Calibration of the Pseudocumene Rotameter</td>
<td>33</td>
</tr>
<tr>
<td>4. Calibration of Thermocouples</td>
<td>34</td>
</tr>
<tr>
<td>B. Experimental Procedure</td>
<td>34</td>
</tr>
</tbody>
</table>
V. RESULTS AND DISCUSSION

A. Experimental Conditions
B. Air Oxidation of Pseudocumene
C. Ammoxidation of Pseudocumene
   1. Vanadium Pentoxide Catalyst
   2. Molybdenum Trioxide Catalyst
D. Ammoxidation of o-Xylene
E. Air Oxidation of Trimellitic Anhydride
F. Ammoxidation of Trimellitic Anhydride
G. Decomposition of Trimellitic Anhydride
H. Sublimation of Phthalic Anhydride

VI. CONCLUSIONS AND RECOMMENDATIONS

REFERENCES
APPENDIX I  Pseudocumene Data
APPENDIX II  Summary of Results of Oxidation of Pseudocumene
APPENDIX III  Calibration Curves for Rotameters
APPENDIX IV  Equipment Specifications
APPENDIX V  Determination of the Critical Diameter of the Reactor

VITA AUCTORIS
FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Schematic Diagram of the Experimental Apparatus</td>
<td>18</td>
</tr>
<tr>
<td>2.</td>
<td>Sectional View of the Reactor</td>
<td>22</td>
</tr>
<tr>
<td>3.</td>
<td>Sectional View of the Preheater</td>
<td>24</td>
</tr>
<tr>
<td>4.</td>
<td>Sectional View of the Carburetor</td>
<td>26</td>
</tr>
<tr>
<td>5.</td>
<td>Sectional View of Pseudocumene Feed Tank</td>
<td>28</td>
</tr>
<tr>
<td>6.</td>
<td>Aromatic Products from a Gulf Coast (U.S.A.) Refinery</td>
<td>61</td>
</tr>
<tr>
<td>7.</td>
<td>Price Variation of Pseudocumene</td>
<td>62</td>
</tr>
<tr>
<td>8.</td>
<td>Calibration Curve for Air Rotameter</td>
<td>63</td>
</tr>
<tr>
<td>9.</td>
<td>Calibration Curve for Ammonia Rotameter</td>
<td>64</td>
</tr>
<tr>
<td>10.</td>
<td>Calibration Curve for Pseudocumene Rotameter</td>
<td>65</td>
</tr>
</tbody>
</table>
# TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Physical Properties of the Catalyst</td>
<td>54</td>
</tr>
<tr>
<td>2. Analysis of Pseudocumene</td>
<td>55</td>
</tr>
<tr>
<td>3. Summary of Observations of Air Oxidation of Pseudocumene</td>
<td>57</td>
</tr>
<tr>
<td>4. Summary of Observations of Ammoxidation of Pseudocumene over Vanadium Pentoxide Catalyst</td>
<td>58</td>
</tr>
<tr>
<td>5. Summary of Observations of Ammoxidation of Pseudocumene over a Molybdenum Trioxide Catalyst</td>
<td>59</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

During World War II, the petroleum industry was called upon to greatly expand its catalytic reforming facilities in order to provide the high octane fuel which was needed for the aircraft engines of the period and also to produce toluene which was needed for the manufacture of TNT. After the war, additional reforming units were added in order to boost the octane rating of automobile gasoline and to supply the rapidly growing domestic and international air travel market.

In the mid-1950's the demand levelled off with the growth in the manufacture of high performance automobile engines which ran on relatively low octane fuels, and in the late 1950's the demand for high octane aviation gasoline rapidly declined with the advent of the jet engine. In the early 1960's the petroleum industry found itself with a large capacity for catalytically reforming petroleum, and a diminishing market for its product.

The large capital investment involved provided the incentive for research in the area of the methyl and the polymethyl benzenes. The bulk of the research
was concentrated on the light aromatics - benzene, toluene, and the 'C₈' aromatics - and numerous applications for them have been found in the production of synthetic fibres and films, plastics, and resins. During this initial period the higher polymethyl benzenes were largely ignored and it is only in the last decade that petroleum companies have realized the great potential of the higher polymethyl benzenes (1).

One of the major problems surrounding the development of the higher polymethyl benzenes was that the products made from them were plastics, plastic coatings, epoxies, and synthetic fibres, and thus they would in effect be competing in an established market. Furthermore, they cost much more than competitive products and initially they apparently did not offer startling use advantages.

The principal reason for the large cost differential was the high cost of the polymethyl benzenes, which were produced by refineries in small amounts as specialty products (2). Large amounts of 'C₉' and 'C₁₀' polymethyl benzenes, together with benzene, 'C₇' and 'C₈' benzenes are found in virgin naphthas, in the products from the catalytic cracker and in the products from the catalytic reformer (Appendix I, Figure 6). At present, the aromatics are not extracted from the catalytic cracker products.
because the high percentage of olefins make separation very difficult.

The aromatics are separated from the reformate stream either by the Udex Process (Universal Oil Products, Dow Chemical extraction process employing a mixture of diethylene glycol, dipropylene glycol, and water), or by double extraction with sulphur wash oil. The aromatics can then be separated from one another by a series of fractional distillations and fractional crystallizations. Pseudocumene is separated from the other 'C_9' components by fractional distillation, and durene is separated from the 'C_{10}' components by a fractional crystallization.

As the amounts of higher polymethyl benzenes produced commercially grew, the unit price dropped rapidly (Appendix I, Figure 7). The price of pseudocumene dropped from $1.50 per pound in 1955 to 8-3/4¢ per pound in 1969. These prices still reflect "limited capacity" production and further price reductions would result if "full capacity" production was initiated. However, pseudocumene recovery, as compared to o-xylene recovery requires an additional fractionation step, and therefore pseudocumene will always be more expensive than o-xylene. The estimated price of o-xylene under "full capacity" recovery conditions would be about 6¢ per pound, as compared to 7¢ per pound for pseudocumene.
The oxidation of benzene, toluene, o-, m-, and p-xylene and naphthalene are all successful commercial processes with ready markets for the products. The oxidation products of pseudocumene and durene which are trimellitic anhydride and pyromellitic dianhydride have been used successfully in the manufacture of plasticizers, alkyd resins for water soluble and 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. It has been found that many of the products made from the oxidized polymethyl benzenes were distinctly superior to those made from the 'C<sub>7</sub>' and 'C<sub>8</sub>' compounds, as the'C<sub>9</sub>' and 'C<sub>10</sub>' anhydrides contain a greater number of free acid groups. It was thus established that pseudocumene could be produced fairly cheaply, and that some excellent products could be obtained from trimellitic acid and trimellitic anhydride (2).

Pseudocumene has been oxidized successfully in the liquid phase, and the "Mid-Century" liquid phase air oxidation process is a commercial process. Amoco Chemical Corporation has constructed a 50 million pound per year plant to produce trimellitic anhydride, but at present is the only producer in the world.
Durene, however, is commercially oxidized by a vapour phase air oxidation process to produce pyromellitic dianhydride. The vapour phase air oxidation of pseudo-cumene, which would parallel the vapour phase air oxidation of o-xylene and durene, would be an ideal alternative route as it would have many advantages over the "Mid-Century" liquid phase process (11). The major advantages would be:

(i) saving on initial plant cost, as the vapour phase process is an atmospheric pressure process while the liquid-phase process is a high pressure process.

(ii) the reactant-catalyst mixture in the liquid phase process combined with reaction conditions results in a highly corrosive mixture. The vapour-phase mixture is only mildly corrosive.

(iii) the vapour phase process is a continuous process, while the liquid-phase process is batch.

(iv) the product separation in the vapour phase process is much easier and cheaper than in the liquid phase process.

(v) the purity of the pseudocumene is not critical in the vapour phase but could result in product contamination in the liquid phase process.
Both o-xylene and durene have been oxidized in the vapour phase, to produce phthalic anhydride and pyromellitic dianhydride respectively:

\[
\text{o-xylene} + 6(0) \xrightarrow{\text{V}_2\text{O}_5} \text{phthalic anhydride} + 3\text{H}_2\text{O}
\]

\[
\text{durene} + 12(0) \xrightarrow{\text{V}_2\text{O}_5} \text{pyromellitic dianhydride} + 6\text{H}_2\text{O}
\]

The important point to be noted is that o-xylene has one pair of methyl groups in the ortho position, and durene has two pairs of methyl groups in the ortho position. The presence of the methyl group in the ortho position appears to facilitate the vapour phase oxidation step. Pseudocumene also has a pair of methyl
groups in the ortho position, and it appears that it should be able to be oxidized in the vapour phase by one of the following steps:

(i)

\[
\text{pseudocumene} \quad \overset{\text{V}_{2}O_{5}}{\xrightarrow{\text{SO}_{3}}} \quad \text{trimellitic anhydride}
\]

or (ii)

\[
\text{pseudocumene} \quad \overset{\text{H}_{2}O}{{\xrightarrow{\text{CH}_{3}}} \text{4-methylphthalic anhydride}}
\]

Rao (4) investigated this system and concluded that pseudocumene could not be oxidized to either of the above products in the vapour phase under the conditions which he used. His reactor, however, displayed large radial temperature profiles, which were eliminated in this study, by use of a new reactor. Some initial runs were made using the same conditions as Rao to
determine whether the elimination of the large radial
temperature profiles resulted in any change in the
products (Appendix V).

O-xylene has been successfully oxidized in the
vapour phase by an ammonia-air mixture, over a vanadium
pentoxide catalyst to produce phthalonitrile.

\[
\text{C}_8\text{H}_8 + 3\text{O}_2 + 2\text{NH}_3 \xrightarrow{\text{V}_2\text{O}_5} \text{C}_8\text{H}_6\text{N}_2 + 6\text{H}_2\text{O}
\]

\text{o-xylene}

M-xylene has also been oxidized in the vapour phase by
the same procedure to produce isophthalonitrile.

\[
\text{C}_8\text{H}_8 + 3\text{O}_2 + 2\text{NH}_3 \xrightarrow{\text{V}_2\text{O}_5} \text{C}_8\text{H}_6\text{N}_2 + 6\text{H}_2\text{O}
\]

\text{m-xylene} \quad \text{isophthalonitrile}

It was expected that the ammoxidation of pseudocumene
could proceed by one of the following paths.
Both 1,2,4-tricyanobenzene and 4-cyano-phthalamide can easily be hydrolyzed to produce trimellitic anhydride.

The objective of the project was to investigate the catalytic vapour phase ammoxidation of pseudocumene using a vanadium pentoxide on inert alumina catalyst and an air-ammonia mixture as the oxidizing agent.
II LITERATURE SURVEY

The vapour phase oxidation of the lower order methyl benzenes has been studied extensively, but there is little information available on the higher poly-methyl benzenes. A review of the available literature on the liquid and vapour phase oxidation of pseudo-cumene and the vapour phase oxidation of o-xylene and durene is presented below. A short review of the vapour phase ammoxidation of o-xylene is also presented.

A. Liquid Phase Oxidation of Pseudocumene

Pseudocumene has been oxidized in the liquid phase to trimellitic acid by the addition of nitric acid to a mixture of pseudocumene and water under pressure (100 psig), and in the presence of HCl, HBr, and alkali metal chlorides such as NH₄Cl and NH₄Br. The nitric acid is added at 160°C and the mixture is heated to 200-250°C. The batch process takes approximately one and a half hours and the yield of trimellitic acid is 89.5% (5,6,7).

Pseudocumene has also been oxidized by a two step process. The first step is a liquid phase air oxidation
under pressure with a cobalt stearate catalyst. The second step involves the addition of water and nitric acid under pressure (100-200 psig) in the presence of HCl and NH₄Cl. This is a batch process with yields of trimellitic acid of 96-97% (8,9). Pseudocumene can also be oxidized in the liquid phase by sulphur dioxide. The process is batchwise. The pressure range is 50-2500 atmospheres, but pressures from 100-400 atmospheres give the best yield. The temperature range is from 200-400°C, but temperatures from 250-350°C give the best yield. Catalysts are not necessary for the reaction but the reaction is promoted by bromine or iodine, and inhibited by metallic copper and silver. The reaction is unaffected by the presence of oxygen and the reaction rate decreases with increasing pressure. When the reaction is carried out at 300°C and 300 atmospheres for 4 hours, the yield of trimellitic acid is 90% (10, 11, 12).

The oxidation of pseudocumene by chromic acid in a glacial acetic acid medium, and by potassium permanganate and sodium hydroxide have also been carried out on a laboratory scale (13).

The base-catalyzed oxidation of pseudocumene to trimellitic acid can be accomplished in the liquid
phase by contacting the pseudocumene with a base such as potassium t-butoxide, or even potassium hydroxide in hexamethylphosphoramide at room temperature and passing oxygen through it. The reaction rates decrease with time. The yield of trimellitic acid after 3 hours is about 10%. (14).

The most successful commercial process for the manufacture of trimellitic acid from pseudocumene is a liquid phase air-oxidation process called the "Mid-Century" process. The process uses a heavy-metal and a form of bromine as a catalyst. The bromine is a regenerable source of chain initiating free radicals. The pseudocumene is dissolved in a suitable solvent, usually acetic acid, and brought to reaction temperature (125-275°C). Pressures up to 40 atmospheres may be used. Air is then passed into the reactor. Oxygen must be in excess of the stoichiometrically required amount. The reaction is highly exothermic, so the reactor must be cooled. The process may be batch, semicontinuous or continuous, but the continuous process gives better yields and product quality. The continuous process however may result in considerable difficulty in temperature control. The yield is 85-90%, but the high temperature combined with the presence of bromine gives rise to a highly corrosive system (15,16).
B. Vapour Phase Oxidation of Pseudocumene

There is very little reported in the literature on the vapour phase oxidation of pseudocumene. In the 7th World Petroleum Congress in Mexico in 1967, Ibing reported that a series of experiments were conducted in the Ruhrol Chemie Werk, West Germany to study the feasibility of the vapour phase oxidation of pseudocumene. The details of the experimental work are not available, but yields of 35-40 percent by weight of trimellitic acid were reported. By-products obtained were 4-methyl phthalic anhydride, maleic anhydride, phthalic anhydride and pyromellitic dianhydride. The isolation and separation of trimellitic anhydride from the by-products is both difficult and expensive (17).

Though he did not directly study the vapour phase oxidation of pseudocumene, Sasayama (18) proposed a series of generalized steps which would describe the vapour phase oxidation of the methyl benzenes. The first step is that the side chain groups are oxidized to the -COOH group one by one. If the heating is continued, the acid looses the -COOH groups one by one and is finally reduced to benzene. Finally, on further oxidation, the benzene ring is cleaved to produce maleic anhydride and carbon dioxide.

The vapour phase oxidation of 1,2,3-trimethylbenzene and 1,2,4-trimethyl benzene, using a vanadium pentoxide
catalyst on pumice stone, promoted with MoO$_3$ was reported by Morita (19). The air flow rate was held constant at 150 litres per hour; the temperature was 400°C; and the hydrocarbon flow rate was 1.5 gm./minute. The catalyst volume was 50 cc. The products for both oxidations were maleic anhydride and carbon dioxide. The yield of maleic anhydride was approximately 3%. No phthalic anhydride or benzoic acid was obtained. Morita suggested that the tricarboxylic acid was formed first, but that as decarboxylation of the extra carbonyl group did not occur, the benzene ring was cleaved and maleic anhydride was formed.

C. Vapour Phase Oxidation of o-xylene

The catalytic vapour phase oxidation of o-xylene has been studied in detail. The experimental conditions vary widely. The hydrocarbon concentration varies from 0.6 to 67 mole percent. The temperature range is 300°C - 650°C. The yields vary from 10-60% (20, 21, 22, 23, 24). Exhaustive studies of various catalysts and comparisons between fixed and fluidized beds have been reported. The most effective catalyst is vanadium pentoxide, and the fluidized bed is found to be more effective than the fixed catalyst bed (25, 26).
The industrial vapour phase oxidation of o-xylene is carried out in a series of large shell and tube reactors. Each reactor contains thousands of tubes filled with catalyst. The ratio of air to o-xylene is 30:1, and the reaction is run at a temperature of 375°C. The yield for this process is 100 lbs of phthalic anhydride per 100 lbs of o-xylene feed. The catalyst is vanadium pentoxide with several undisclosed inhibitors (27, 28).

D. Vapour Phase Oxidation of Durene

The vapour phase oxidation of durene is very similar to that of o-xylene. The catalyst is vanadium pentoxide, and the durene to air ratio is 1:6 by weight. The reaction temperature is 450–535°C. Contact time varies from 0.1 sec - 1.0 sec., and yields of 50 to 90% of pyromellitic dianhydride have been reported (29, 30, 31).

E. Ammoxidation of o-xylene

The ammoxidation of o-xylene is very similar to the vapour phase air oxidation of o-xylene. The reaction conditions are as follows: o-xylene: O₂: NH₃ (molar ratio) is 1:5:25 to 1:5:5:16; reaction temperature 400–450°C. Contact times are from 0.2 to
0.6 secs., and catalysts used are 5% V₂O₅, 5% V₂O₅ plus 9.6% K₂SO₄, 5% V₂O₅ plus 0.3% MoO₃. The major product is phthalonitrile with o-tolunitrile, benzonitrile and phthalimide as side products. The industrial process is basically a scale up of the laboratory procedure (32, 33, 34). Hadley suggests that the route followed during ammoxidation is the production of the acid corresponding to the hydrocarbon, (phthalic acid from o-xylene); after that he suggests the production of the imine, and finally the nitrile is produced. The suggested reaction is as follows:

\[
\begin{align*}
R-CH_3 & \xrightarrow{O_2} RCOOH \xrightarrow{NH_3} RCOONH_4 \xrightarrow{} RCN.
\end{align*}
\]

This path appears to be of general validity for ammoxidation of alkyl aromatics (35).
III EXPERIMENTAL EQUIPMENT

The equipment was constructed so that either vapour phase air oxidations or vapour phase ammoxidations with air-ammonia mixtures as the oxidizing agents could be studied.

The oxidation products were identified by gas chromatographic analysis. The description of the experimental set up and the major individual components of the system is given below. The specifications of all other equipment are given in Appendix IV.

A. Flow Diagram

The experimental equipment consisted of an air feeding system, an ammonia feeding system and a pseudo-cumene feeding system, an air preheater, a carburetor and a reactor, a system of condensers and various temperature, pressure, flow measurement and heating devices. The details of the flow system are given in Figure 1. Compressed air at 90-100 psig from the laboratory compressed air line was passed through an air filter with a stone filter screen in order to remove impurities such as oil or dirt from the air.
CV: CHECK VALVE
NV: NEEDLE VALVE
GV: GATE VALVE
TC: THERMOCOUPLE
PR: PRESSURE REGULATOR
R: ROTAMETER

FIG. 1 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS
The clean air was passed through a low pressure regulator (PR1) to reduce it to the required range of 5-10 psig. The air was then passed through a rotameter (R2) of 0-60 SCFH air capacity, where the flow rate was monitored. The flow rate was controlled by a needle valve (NV4). The air was preheated to 350-450°C in an electrically heated air preheater prior to entering the carburetor where it was mixed with the other reactants. Pseudo-cumene was pressure fed to the carburetor by nitrogen displacement from the feed tank. The nitrogen pressure was maintained at 16 psig by means of a two stage regulator (PR2). The flow rate of the pseudocumene was monitored by a rotameter (R1) of 0-32 cc/min capacity and controlled by a needle valve (NV3). In the second series of experiments when ammonia was used, the ammonia was passed into the carburetor through a low pressure regulator (PR3) to reduce the pressure to the required range of 5-10 psig. The ammonia flow rate was obtained from a rotameter (R3) of 0-100 SCFH ammonia capacity, and controlled by a needle valve (NV5). The carburetor, an electrically heated cylindrical vessel packed with one-quarter inch berl saddles served two purposes. It thoroughly mixed the reactants, and it also brought them to the
reaction temperature. On leaving the carburetor the mixture entered the integral reactor. The reactor was heated electrically by three independent heaters, and had three distinct zones:

(i) preheating zone
(ii) reaction zone
(iii) buffer zone

The preheating zone and the buffer zone were packed with one-quarter inch berl saddles, and the reaction zone was packed with the catalyst. The preheating zone was used to bring the reacting mixture up to the desired temperature of 350-450°C. The reaction was highly exothermic, so that once the reaction started, the external heat supplied to the reactor had to be reduced in order to maintain isothermal conditions across the reaction zone. Due to heat losses at the end of the reactor, that section of the reactor exhibited large temperature fluctuations and uneven temperature distribution. The buffer zone of berl saddles was added so that the uneven temperatures in this area did not affect the reaction zone. The oxidation products were condensed by a system of three water-cooled condensers in series. The temperature was measured at nine different locations in the system, by means of ungrounded chromel-alumel thermocouples (TC1-TC9).
B. Details of Equipment

1. Reactor

The reactor was constructed from a 1/4 inch section of 1-1/2 inch schedule 40, 304 stainless steel pipe. The ends of the pipe were welded to 300 psig welding neck flanges, and matching blind flanges completed the body of the reactor. The details of the reactor are shown in Figure 2. Aluminium gaskets, 1/8 inch thick, 2 inch I.D. and 3 inch O.D. were used to obtain leakproof joints. Two 1/8 inch O.D., 3-3/4 inch long stainless steel thermowell tubes were welded to the top flange, as was a 3/8 inch tube to insert berl saddles into the reactor. A 1/4 inch stainless steel swagelok male connector was inserted through the centre of the top blind flange to serve as the inlet to the reactor. Two 1/8 inch O.D., 3-3/4 inch long stainless steel thermowell tubes were welded to the bottom blind flange. A 1/8 inch stainless steel swagelok male connector was inserted through the centre of the bottom blind flange in order to allow a 1/8 inch O.D. stainless steel thermowell tube to be inserted to various lengths into the reactor.

The reactor bed consisted of a stainless steel sleeve, 5-1/2 inches long, with an O.D. of 1-3/8 inches. The ends of the sleeve were closed with stainless steel screens, 1/16 inch thick, which fitted tightly to the
FIG. 2 SECTIONAL VIEW OF THE REACTOR
reactor tube. The sleeve was filled with a mixture of the catalyst and inert alumina beads. The screens had 1/8 inch holes drilled in them in order to allow the insertion of the thermowell tubes into the catalyst mass. The sleeve was placed 1-1/2 inches from the bottom of the reactor, and the rest of the reactor was filled with 1/4 inch berl saddles.

The reactor was heated by three independently controlled semicylindrical heating units of 3-1/2, 5, and 3-1/2 inches length respectively, and rated at 700, 1160, and 700 watts respectively. The voltage applied to each heating element was controlled by means of a variable transformer. The reactor unit was insulated with glass wool.

2. Air Preheater

The construction of the body of the air preheater was exactly the same as that of the reactor (see Figure 3) except that an 18 inch section of schedule 40 stainless steel pipe was used. Two 1/8 inch O.D., 4 inch long stainless steel thermowell tubes were welded to both the top and bottom blind flanges. The preheater was completely packed with 1/4 inch berl saddles and was heated by two 12 inch long semicylindrical heating units, connected in parallel.
FIG. 3 SECTIONAL VIEW OF THE PREHEATER.
Each of these units was rated at 700 watts and the power input was controlled by a variable transformer. The air preheater was insulated with glass wool.

3. Carburetor

The carburetor was constructed from an 11 inch section of 2 inch nominal diameter, schedule 40 carbon steel pipe (Figure 4). The top end was welded to a 2 inch diameter, 150 psig standard pipe flange, and closed with a matching blind flange. Three stainless steel 1/4 inch swagelok male connectors were inserted in the blind flange to serve as inlet ports for the preheated air, ammonia, and pseudocumene. A 1/8 inch thick, 1-1/2 inch I.D., 2-1/2 inch O.D. copper gasket was used to give a leakproof joint. The bottom end of the carburetor was closed by welding on a 3 inch diameter, 1/2 inch thick steel plate. A 1/4 inch stainless steel swagelok male connector was inserted through the centre of the bottom to serve as an exit port for the preheated reactants. The carburetor was filled with 1/4 inch berl saddles to promote mixing, and was heated by two 8 inch long semicylindrical heating units connected in parallel. Each of the units was rated at 500 watts and the power input to the heaters was controlled by
FIG. 4 SECTIONAL VIEW OF THE CARBURETOR.
means of a variable transformer. The carburetor was completely insulated with glass wool.

4. Pseudocumene Feeding System

The pseudocumene feed tank was constructed from a 15 inch long section of 5 inch nominal diameter, schedule 40 mild steel pipe (Figure 5). The bottom end of the tank was completely closed by welding on a 6 inch diameter, 1 inch thick plate. The top end of the tank was welded to a standard 5 inch diameter flange, and closed with a matching blind flange. A 1/4 inch thick, 3 inch I.D., 4-1/2 inch O.D. neoprene rubber gasket was used to obtain a leak free joint. Three 1/4 inch brass swagelok male connectors were tapped to the blind flange to serve as the nitrogen line, the pseudocumene discharge line and the air purge line. In addition a 1/2 inch brass swagelok male connector with a plug end was inserted to provide for feeding pseudocumene to the tank. The 1/4 inch copper pseudocumene feed line extended to within 1/2 inch of the tank bottom.

C. Catalyst

The catalyst used was a commercial grade vanadium pentoxide catalyst, supported on inert alumina, supplied
FIG. 5 SECTIONAL VIEW OF PSEUDOCUMENE FEED TANK
by M/S Harshaw Chemical Company, Cleveland, Ohio, U.S.A.
The catalyst had a low surface area to mass ratio, and
was chosen because this type of catalyst had previously
been used successfully for the vapour phase oxidation
of o-xylene to phthalic anhydride and durene to pyro-
mellitic dianhydride. The physical properties of the
catalyst are given in Table 1, in Appendix I.

D. Raw Materials

Pseudocumene used in the experiments came from two
sources. In most instances the pseudocumene used 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 2, Appendix I. In certain selected cases
pseudocumene of certified grade from the Aldrich
Chemical Company, Inc., Milwaukee, Wisconsin was used.
Trimellitic anhydride, trimellitic acid, phthalic
anhydride and maleic anhydride used for calibration
purposes were of Fisher Highest Purity grade from the
Fisher Scientific Company. Phthalonitrile, phthalimide,
phthalamide, o-toluamide, o-tolunitrile, benzonitrile
and maleic imide used for calibration purposes were
of Fisher Highest purity grade.
E. Analytical Equipment

The product stream was analysed using a Varian Aerograph series 1520, dual column gas chromatograph. The sensing element used was a thermal conductivity detector. The signals from the thermal conductivity detector were recorded on a Varian Aerograph model 30 strip chart recorder.

1. Air Oxidation of Pseudocumene

A column suitable for the analysis of the aromatic anhydrides up to and including the 'C⁹' anhydrides could not be found. However, two columns were found which would separate the aromatic anhydrides up to and including the 'C₈' anhydrides. The first of these two columns was a 10 foot by 1/4 inch stainless steel column packed with 10% Bis (2-ethylhexyl tetra-chlorophthalate) on 60/80 mesh, acid washed, dimethyl-chlorosilane treated chromosorb W. The second column was a 10 foot by 1/8 inch stainless steel column packed with 8% F.F.A.P. on 60/70 mesh acid washed, dimethyl-chlorosilane treated chromosorb W supplied by Varian Aerograph. The second column gave better separation and was therefore the column used for the analysis. Since trimellitic acid and anhydride are solids at
room temperature with very low solubilities in pseudocumene (while pseudocumene is a liquid), the appearance of a solid in the glass condenser system would be a clear indication of the presence of these products in the reactor effluent. The absence of a solid in the condenser was taken to be an indication that no trimellitic acid or anhydride was produced.

2. Ammoxidation of Pseudocumene

As was the case with the air oxidation of pseudocumene, a column suitable for the analysis of the 'C₉' ammoxidation products could not be found. The 10 foot by 1/8 inch stainless steel column packed with 8% F.F.A.P. on 60/70 mesh acid washed, dimethylchlorosilane treated chromosorb W could separate the aromatic ammoxidation products up to and including the 'C₈' products. The 'C₉' aromatic ammoxidation products are solids at room temperature, with low solubilities in pseudocumene. The appearance of a solid would be an indication of the presence of either 1,2,4-tricyanobenzene or 4-cyanophthalimide. The absence of a solid in the condenser was taken to be an indication that no 1,2,4-tricyanobenzene or 4-cyanophthalimide was produced.
IV EXPERIMENTAL PROCEDURE

A. Calibration Procedure

1. Calibration of the Air Rotameter

The air rotameter was calibrated directly by using a wet test gas meter, supplied by the Precision Scientific Company. Inlet pressure and temperature conditions were used for this calibration. The volumetric flow rates at the conditions of calibration were then converted to standard conditions (14.7 psia, 70°C) so that this 'standard curve' could be used to determine the flow rates for various inlet pressure conditions. Since the major components of air (N₂, O₂) are practically insoluble in water, the presaturator of the wet test meter was filled with distilled water. The calibration curve is given in Appendix III, Figure 8.

2. Calibration of the Ammonia Rotameter

The ammonia rotameter could not be directly calibrated using the wet test meter, because ammonia is very soluble in water. The indirect calibration
was carried out as follows. The rotameter was first directly calibrated using nitrogen gas and the precision wet test meter. The inlet pressure and temperature were used for this calibration. The flow rate was then converted to standard conditions, and the ammonia flow rate at standard conditions was computed using the density correction factor (\(\sqrt{\frac{\rho_{\text{ammonia}}}{\rho_{\text{nitrogen}}}}\)). Ammonia was then run through the rotameter and dissolved in a known volume of water for a specific time. The solution was then titrated with a standard solution of HCl, and the ammonia flow rate was computed. The experimental value of the ammonia flow rate agreed with the computed value to within ± 5%. The calibration curve is given in Appendix III, Figure 9.

3. Calibration of the Pseudocumene Rotameter

The pseudocumene rotameter was calibrated by measuring the volume of pseudocumene collected in a burette for a fixed time. Since the effects of small temperature and pressure changes on liquids are negligible, the values of the flow rate obtained at room temperature and pressure were used for the entire experimental range. The calibration curve is given in Appendix III, Figure 10.
4. Calibration of Thermocouples

The chromel-alumel thermocouples used were of the ungrounded type. The ungrounded thermocouples were used because the A.C. current employed by the electrical heaters caused an induced e.m.f. (up to 2 mV) to accumulate in the system. If grounded thermocouples had been used, the induced e.m.f. would have resulted in inaccurate temperature measurement. The accuracy of the thermocouples was checked against the ice point (0°C) and the melting point of pure tin (231.85°C). All the thermocouples were accurate to ± 0.5°C.

B. Experimental Procedure

The reactor was charged with the required amount of catalyst, and then air from the compressed air line was turned on and controlled by the fine needle control valve at the outlet of the rotameter. The heaters for the reactor, carburetor and air-preheater were then turned on and allowed to reach steady state. The desired steady state temperatures were obtained by adjusting the respective variable transformers. The system took approximately four hours to reach steady state at 400°C. For the air oxidation experiments, pseudocumene was fed to the carburetor by pressurizing the feed tank with
nitrogen to 16 psig. For the ammoxidation experiments, ammonia was fed to the carburetor at the desired flow rate and the system was allowed to reach steady state before the pseudocumene was fed to the carburetor. The pseudocumene flow rate was controlled by the needle valve on the rotameter. Once the desired flow rates of air, ammonia (if needed) and pseudocumene had been established, the system was allowed to run for approximately 15 minutes so that a position of dynamic equilibrium could be attained. At this point the system of condensers was attached to the reactor exit line, and the experiment was allowed to run for one hour. Once the reaction was running, the heat supplied to the reactor was reduced to maintain isothermal conditions in the catalyst bed. For the duration of the run, the reactor temperatures were frequently checked. At the end of the run the liquid condensate and any solid deposited in the condenser tubes were collected for subsequent analysis. In order to shut down the reactor, the pseudocumene flow was shut off, and the feed tank was depressurized. The valve was then reopened and the pseudocumene in the lines was allowed to drain back into the feed tank. The ammonia flow was then shut off. The air flow was allowed to
continue until the system was back at room temperature. The feed tank was depressurized after shutdown so that nitrogen would not dissolve in the pseudocumene. The dissolved nitrogen would then come back out of solution and appear as slugs of gas in the pseudocumene flow through the rotameter due to reduction of pressure after the flow through the needle valve.
V RESULTS AND DISCUSSION

The vapour phase air oxidation of pseudocumene was studied in detail by Rao (4), using the same apparatus. During the initial phase of this project, a thermocouple was inserted in the centre of the reactor and under the experimental conditions used by Rao, temperature differences between the centre and the side of the reactor were observed to be as high as 80°C. A steel sleeve was inserted into the reactor and this reduced the internal diameter of the reaction zone to 1 inch. With this change in design it was observed that the conditions which had initially produced an 80°C radial temperature difference now only produced a 10°C radial difference. Experimental runs for the air oxidation of pseudocumene were made, duplicating the experimental conditions used by Rao in order to determine the effect of the reduction of the radial temperature gradient.

A. Experimental Conditions

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

37
(i) reaction temperatures of 350-450°C
(ii) vanadium pentoxide catalyst, 50 grams
(iii) molybdenum trioxide catalyst, 50 grams
(iv) pseudocumene feed
(v) air oxidation, molar oxygen to pseudocumene ratio of 30:1
(vi) ammoxidation, molar pseudocumene to oxygen to ammonia ratios of 1:5:15; 1:5:20; and 1:5:25
(vii) ammoxidation, molar o-xylene to oxygen to ammonia ratios of 1:5:15; 1:5:20; and 1:5:25
(viii) constant air flow rate of 30 SCFH, which corresponds to a contact time of about 0.2 seconds.

In order to determine whether trimellitic anhydride was initially formed and subsequently oxidized further, trimellitic anhydride dissolved in acetone was fed to the reactor in the presence of air and also air-ammonia mixtures. Finally to determine whether trimellitic anhydride and phthalic anhydride sublime or decompose, pure samples of each were slowly heated and the effluent gasses were monitored for carbon dioxide. A summary of the various experimental results is given in subsequent sections under the following headings:
B. Air Oxidation of Pseudocumene

Experimental runs were conducted with a constant catalyst weight of 50 grams of vanadium pentoxide, and constant molar ratio of oxygen to pseudocumene of 30:1. Runs were made for reaction temperatures of 350°C, 370°C, 390°C, 400°C, 410°C, 430°C, and 450°C. At 350°C and 370°C, no solid deposit was observed in the condenser and the condensate was a very pale yellow colour and single phase. The condensate was found to be pseudocumene by gas chromatography analysis which indicated that no oxidation was taking place. At all temperatures higher than 370°C, no solid deposit was observed in the condenser, but the liquid condensate had two distinct layers. The top layer was pale yellow and accounted for 80-90 percent of the volume. This was determined
to be pseudocumene. The bottom layer was a light brown colour at 390°C, and the colour became darker as the temperature was raised. These observations are in agreement with the findings of Miller (29, 30) and Rao (4). The dark brown layer was analyzed by gas chromatography and the constituents were determined to be pseudocumene, maleic anhydride and water. This is in agreement with the findings of Morita (19). There was a white exhaust from the condenser in all the trials, even though the exit temperature of the exhaust was approximately 10°C. This was probably due to the formation of a eutectic mixture of air and pseudocumene which required a very low temperature for complete condensation of pseudocumene. The catalyst weight of 50 grams was chosen because Rao (4) determined in a previous study that the optimum catalyst loading for this particular reactor was approximately 40-50 grams.

C. Ammoxidation of Pseudocumene

1. Vanadium Pentoxide Catalyst

The pseudocumene ammoxidation was carried out over a 50 gram charge of vanadium pentoxide catalyst, and with molar ratios of pseudocumene to oxygen to ammonia of 1:5:15; 1:5:20; and 1:5:25. The reaction was carried out at temperatures of 350°C, 400°C and 450°C.
No solid deposit was observed for any of the reaction conditions. At 350°C, the liquid condensate was single phase, and light yellow in colour. By gas chromatography, it was determined to be unreacted pseudocumene. At 400°C and molar ratio of pseudocumene to oxygen to ammonia of 1:5:15, the liquid condensate had two distinct layers. The bottom layer was yellow and was about 80% of the volume. This layer was determined to be unreacted pseudocumene. The top layer was brown and on analysis it was found to be composed of maleic imide, pseudocumene and water. At 400°C as the ammonia flow rate was increased, the colour of both layers became lighter, but the analysis of the product yielded the same results. At 450°C, the liquid condensate was two layers, the bottom layer being about 70-80 percent of the total, of a dark yellow colour. As the ammonia flow rate was increased, the colour again became lighter. This layer was pseudocumene. The top layer was a dark brown, which became lighter as the ammonia flow rate was increased. The analysis yielded the same results as those for 400°C.

2. Molybdenum Trioxide Catalyst

The pseudocumene ammoxidation was run over a 50 gram charge of molybdenum trioxide (20% molybdenum trioxide on inert alumina) with a molar ratio of pseudo-
cumene to oxygen to ammonia of 1:5:20. Reaction temperatures of 350°C, 400°C, and 450°C were maintained. The molybdenum trioxide catalyst was used in place of vanadium pentoxide as the former catalyst involves a milder oxidation.(26). No solid deposit was observed under any of the reaction conditions tried. In all cases, the liquid condensate was two distinct layers. The bottom layer, which was about 98 percent of the condensate, was determined to be pseudocumene. The top layer, which was about 2 percent of the condensate, became darker in colour as the reaction temperature was increased, but by gas chromatography analysis it was determined that it contained maleic imide, water and pseudocumene. Thus, the ammoxidation of pseudocumene over a vanadium pentoxide catalyst, and over molybdenum trioxide catalyst gave the same product. However, the amount of pseudocumene oxidized over the latter catalyst under identical conditions is much less than over the former.

D. Ammoxidation of o-Xylene

The o-xylene ammoxidation was carried out over a 50 gram mass of vanadium pentoxide catalyst. Molar ratios of o-xylene to oxygen to ammonia of 1:5:15; 1:5:20; and 1:5:25 were used, and reaction temperatures of 380°C, 400°C and 420°C were employed. In all cases,
a crystalline solid was observed in the condenser tube. At 380°C and the molar ratio of 1:5:25, the solid was light brown. As the temperature was increased the solid became darker and the crystals were smaller. As the ratio of ammonia to o-xylene was decreased, the solid also became darker. In all cases the liquid condensate collected consisted of two distinct layers. The top layer, which was about 80 percent of the condensate, was light brown in colour, and was determined to be mainly unreacted o-xylene, with trace amounts of benzonitrile and o-tolunitrile. The bottom layer was dark brown at high ammonia flow rates and 380°C, and became darker as the temperature was increased and the ammonia flow rate was decreased.

Gas chromatography analysis of the products yielded the following results: the bottom layer of the liquid contained o-xylene, o-tolunitrile, benzonitrile, water, and a trace amount of phthalonitrile; the solid deposited in the condenser tubes was determined to be phthalonitrile. These observations are in agreement with the work of Ogata and Sakanishi (32), except that in this case, no phthalimide was observed.
E. Air Oxidation of Trimellitic Anhydride

A 25 percent by weight solution of trimellitic anhydride in acetone was fed to the reactor over a 50 gram vanadium pentoxide catalyst. The air flow rate was kept constant at 30 SCFH, and reactor temperatures of 400°C, 420°C and 450°C were maintained. No solid was observed in the condenser, and the liquid condensate was one phase and light yellow in colour. The exhaust gases contained a high percentage of carbon dioxide and was free of condensable vapour. When the condensate was analyzed by gas chromatography, it was determined to be almost exclusively water with a trace amount of maleic anhydride. This is in agreement with Morita (19) and Sasayama (18), though the maleic anhydride obtained in this case is far less than the 3 percent obtained by Morita. This result means that the benzene ring is cleaved during the reaction. Morita suggested that trimellitic acid was first formed and then was further oxidized to maleic anhydride and carbon dioxide.

F. Ammoxidation of Trimellitic Anhydride

A 25 percent solution by weight of trimellitic anhydride in acetone was fed to the reactor. The flow rate was maintained at a level such that the molar ratio of trimellitic anhydride to oxygen to ammonia was
The air flow rate was maintained at 30 SCFH. The catalyst was 50 grams of vanadium pentoxide and runs were made with reaction temperatures of 400°C, 420°C, and 450°C. No solid deposit was observed in the condenser, and the liquid condensate was pale yellow in colour and one phase. The vapour exhaust was free of condensable vapours and contained a high percentage of carbon dioxide. The condensate was analyzed by gas chromatography and was found to be almost exclusively water with a trace amount of maleic anhydride. This means that ring cleavage occurs, and suggests that the ammonia has no effect on the reaction once the anhydride has been formed as the products were exactly the same as for the air oxidation of trimellitic anhydride.

G. Decomposition of Trimellitic Anhydride

A pure sample of trimellitic anhydride was heated slowly in a 6 x 1/2 inch test tube which in turn was placed in a boiling tube. The boiling tube was externally heated with a heating tape. The temperature of the trimellitic anhydride was monitored with a pair of ungrounded chromel alumel thermocouples. As the temperature was raised the trimellitic anhydride began to decompose very slowly at 265°C. This was determined by testing the exhaust gas for carbon dioxide. At 280°C,
the decomposition rate was fairly rapid. The trimellitic anhydride was maintained at 280°C until the stream of carbon dioxide ceased. The solid residue in the tube was analyzed by gas chromatography and was determined to be phthalic anhydride. Thus, even at the fairly low temperature of 265°C, the trimellitic anhydride released the carbon dioxide group in the fourth position on the benzene ring.

H. Sublimation of Phthalic Anhydride

A pure sample of phthalic anhydride was heated slowly in the same system that was used for trimellitic anhydride. During the heating process, no carbon dioxide was found in the exit gas. In the temperature range of 285-290°C, sublimation occurred and the vapours condensed on the upper, unheated end of the test tube in the form of thin, needle-like crystals. When samples of these crystals were analyzed on the gas chromatograph, it was determined that they were phthalic anhydride. Thus, phthalic anhydride sublimes on heating above 285°C, and does not decompose.
VI CONCLUSIONS AND RECOMMENDATIONS

The results obtained for the air oxidation of pseudocumene over a vanadium pentoxide catalyst and using the modified reactor confirmed the findings of Rao (4). Pseudocumene could not be oxidized for the range of the reaction conditions studied without rupture of the benzene ring. The products were maleic anhydride and water. Under similar reaction conditions trimellitic anhydride was shown to oxidize totally to carbon dioxide and water. A possible sequence of reactions for the air oxidation of pseudocumene is as follows:

\[
\text{pseudocumene} + \text{oxygen} \rightarrow \text{trimellitic acid}
\]

\[
\text{dehydration} \rightarrow \text{trimellitic anhydride} \quad \text{rupture of benzene ring}
\]

\[
\text{malic acid} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{maleic anhydride}
\]
However, this scheme does not explain the absence of maleic anhydride as a product in the air oxidation of trimellitic anhydride.

With the same vanadium pentoxide catalyst but with air-ammonia as the oxidizing medium, pseudocumene decomposed into maleic imide and water. Similar results were obtained with molybdenum trioxide as catalyst.

On the basis of air oxidation results obtained so far, it would appear that pseudocumene oxidation is not controllable under reaction conditions studied and the catalysts tried. One reason for this may well be that trimellitic anhydride, even if formed, is likely to be unstable for temperatures above 300°C. Under milder ammoxidation conditions, benzene and ring rupture is still not avoided. Search for a catalyst which can provide high enough reaction rates at temperatures below the conditions so far tested would seem therefore to be a worthwhile undertaking.
REFERENCES


APPENDIX I

Pseudocumene Data
Physical Properties of the Catalyst

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td></td>
</tr>
<tr>
<td>1. Type</td>
<td>Vanadia oxidation Catalyst V-0501 S- 0.25 inch</td>
</tr>
<tr>
<td>2. V\textsubscript{2}O\textsubscript{5} Content</td>
<td>10 %</td>
</tr>
<tr>
<td>3. Apparent Bulk Density</td>
<td>80 lbs/cu ft</td>
</tr>
<tr>
<td>4. Surface Area</td>
<td>1.0 sq m/gm</td>
</tr>
<tr>
<td>5. Size</td>
<td>0.25 in. spheres</td>
</tr>
</tbody>
</table>

| **B** |   |
| 1. Type | molybdenum trioxide |
| 2. MoO\textsubscript{3} Content | 20 % |
| 3. Size | 0.25 in. spheres |
Analysis of Pseudocumene

1. API gravity @ 60°F (ASTM - D287) 29.4
2. Specific gravity @ 60°F 0.8796
3. Freezing point, °F -47
4. Flash point (ASTM - TCC) °F 121
5. Explosive limits: Upper 6.0
   Lower 1.0
6. Refractive index @ 20°C 1.5045
7. Colour (ASTM - D156) +30
8. Doctor test sweet
9. Corrosion (ASTM - D130) pass
10. Corrosion (full distillation) pass
11. Neutrality of residue neutral
12. Distillation (ASTM)

<table>
<thead>
<tr>
<th>I.B.P.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>336</td>
</tr>
<tr>
<td>10%</td>
<td>337</td>
</tr>
<tr>
<td>20%</td>
<td>337</td>
</tr>
<tr>
<td>30%</td>
<td>337</td>
</tr>
<tr>
<td>40%</td>
<td>337</td>
</tr>
<tr>
<td>50%</td>
<td>337</td>
</tr>
<tr>
<td>60%</td>
<td>337</td>
</tr>
<tr>
<td>70%</td>
<td>337</td>
</tr>
<tr>
<td>80%</td>
<td>337</td>
</tr>
<tr>
<td>90%</td>
<td>337</td>
</tr>
<tr>
<td>95%</td>
<td>337</td>
</tr>
</tbody>
</table>

13. Dry end point 338
14. Distillation recovery 98.5%
15. Distillation residue 1%
16. Distillation loss 0.5%
APPENDIX II

Summary of Results of Oxidation of Pseudocumene
Table 3: Summary of Observations of Air Oxidation of Pseudocumene

<table>
<thead>
<tr>
<th>Catalyst (gm)</th>
<th>Temp. (°F)</th>
<th>Molar Oxygen to H.C. Ratio</th>
<th>Solid Deposit</th>
<th>Liquid Condensate</th>
</tr>
</thead>
<tbody>
<tr>
<td>vanadium pentoxide (50 gm)</td>
<td>350</td>
<td>30 : 1</td>
<td>none</td>
<td>one phase - light yellow; G.C. analysis: pseudocumene</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>30 : 1</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>vanadium pentoxide (50 gm)</td>
<td>390</td>
<td>30 : 1</td>
<td>none</td>
<td>two layers: 90% light yellow top layer; 10% light brown bottom layer. G.C. analysis: top layer pseudocumene; bottom layer: maleic anhydride, water &amp; pseudocumene. As temperature increases both the top and the bottom layers become darker in colour. The G.C. analysis yields the same qualitative results.</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>30 : 1</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td></td>
<td>410</td>
<td>30 : 1</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td></td>
<td>430</td>
<td>30 : 1</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>30 : 1</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>Catalyst (gram)</td>
<td>Temp. (°F)</td>
<td>Molar H.C.:O₂:NH₃ Ratio</td>
<td>Solid Deposit</td>
<td>Liquid Condensate</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------</td>
<td>-------------------------</td>
<td>---------------</td>
<td>------------------</td>
</tr>
<tr>
<td>vanadium pentoxide (50 gm)</td>
<td>350</td>
<td>1:5:15</td>
<td>none</td>
<td>one layer, light yellow in colour. G.C. analysis: pseudocumene. No reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:5:20</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:5:25</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>vanadium pentoxide (50 gm)</td>
<td>400</td>
<td>1:5:15</td>
<td>none</td>
<td>two layers, 80% yellow bottom layer; 20% top brown layer. G.C. analysis: bottom layer: pseudocumene; top layer: maleic imide, pseudocumene &amp; water.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:5:20</td>
<td>none</td>
<td>same as above, except colours of both layers lighter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:5:25</td>
<td>none</td>
<td>same as above, except colours of both layers lighter</td>
</tr>
<tr>
<td>vanadium pentoxide (50 gm)</td>
<td>450</td>
<td>1:5:15</td>
<td>none</td>
<td>two layers: 70-80% dark yellow bottom layer; 20-30% dark brown top layer. G.C. analysis: bottom: pseudocumene; top: maleic imide, pseudocumene &amp; water.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:5:20</td>
<td>none</td>
<td>same as above, except colours of both layers lighter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:5:25</td>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Summary of Observations of Ammoxidation of Pseudocumene over Vanadium Pentoxide Catalyst

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (°F)</th>
<th>Molar H.C.:O₂:NH₃ Ratio</th>
<th>Solid Deposit</th>
<th>Liquid Condensate</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₃ (50gm)</td>
<td>350</td>
<td>1:5:20</td>
<td>none</td>
<td>two layers: 98% light yellow bottom layer; 2% light brown top layer. G.C. analysis: bottom: pseudocumene; top: maleic imide, water &amp; pseudocumene</td>
</tr>
<tr>
<td>MoO₃ (50gm)</td>
<td>400</td>
<td>1:5:20</td>
<td>none</td>
<td>two layers: 98% light yellow bottom layer; 2% light brown top layer. G.C. analysis: bottom: pseudocumene; top: maleic imide, water, &amp; pseudocumene</td>
</tr>
<tr>
<td>MoO₃ (50gm)</td>
<td>450</td>
<td>1:5:20</td>
<td>none</td>
<td>two layers: 98% light yellow bottom layer; 2% brown top layer. G.C. analysis: Bottom: pseudocumene; top: maleic imide, water, &amp; pseudocumene</td>
</tr>
</tbody>
</table>

Table 5: Summary of Observations of Ammoxidation of Pseudocumene over a Molybdenum Trioxide Catalyst.
APPENDIX III

Calibration Curves for the Rotameters
FIG. 6 AROMATIC PRODUCTS FROM A GULF COAST (USA) REFINERY
FIG. 7 PRICE VARIATION OF PSEUDOCUMENE
Fig. 8: CALIBRATION CURVE FOR AIR ROTAMETER
Fig. 9: CALIBRATION CURVE FOR AMMONIA ROTAMETER
Fig. 10: CALIBRATION CURVE FOR PSEUDOCUMENE ROTAMETER
APPENDIX IV

Equipment Specifications
Equipment Specifications

1. **Air Filter**

   - **Make:** Trerice and Company
   - **Type:** Model No. 40
   - **Capacity:** 275 CFM at 80-100 lbs air (Max)
   - **Maximum pressure:** 300 psig
   - **Filter Screen:** stone

2. **Low Pressure Regulator** (PR1 in Figure 1)

   - **Make:** Matheson of Canada Ltd.
   - **Type:** Model No. 70A
   - **Inlet Pressure:** Maximum 250 psig
   - **Outlet Pressure:** 5-10 psig
   - **Delivery Pressure Gauge:** 0-30 psig
   - **Inlet Hose Connection:** Matheson reinforced butyl rubber hose to withstand 2500 psig.

3. **Two Stage Regulator** (PR2 in Figure 1)

   - **Make:** Matheson of Canada Ltd.
   - **Type:** Model No. 1L
   - **Inlet Pressure:** Maximum 2400 psig
   - **Outlet Pressure:** 3-80 psig
   - **Delivery Pressure Gauge:** 0-100 psig
   - **Cylinder Pressure Gauge:** 0-3000 psig

67
4. **Low Pressure Regulator** (PR3 in Figure 1)
   - **Make:** Matheson of Canada Ltd.
   - **Type:** Model No. 71A
   - **Inlet Pressure:** Maximum 250 psig
   - **Outlet Pressure:** 5-10 psig
   - **Delivery Pressure Gauge:** 0-15 psig

5. **Air Rotameter** (0-60 SCFH)(R2 in Figure 1)
   - **Make:** Schutte and 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

6. **Air Rotameter** (0-300 SCFH)(Alternate for R2 in Figure 1)
   - **Make:** Schutte and Koerting Co.
   - **Type:** 'Safeguard' rotameter, series 1800 with 'HFC' high capacity fluted tube
   - **Meter Size:** 3
   - **Tube No.:** 3 - HCFb
   - **Float No.:** 34 - J, stainless steel
   - **Scale:** 250 mm
   - **Capacity:** 5 - 46 CFM air at 70°F and 14.7 psia
7. **Air Control Valve** *(NV4 in Figure 1)*

Make: Matheson of Canada Ltd.
Type: Model No. 940B (Instrument type metering valve)
Body: Brass
Packing: Buna - N

8. **Check Valves** *(CV1, CV2, and CV3 in Figure 1)*

Make: Matheson of Canada Ltd.
Capacity: 100 SCFH air at 10 psig inlet pressure
Maximum Pressure: 2000 psig
Cracking Pressure: approximately 1 psig
Duty Model Material of Construction
Air (CV1) 400-X Brass, neoprene o-ring, stainless steel spring
Ammonia (CV3) 401-X stainless steel 303*, viton-o-ring, stainless steel spring
Pseudocumene (CV2) 401-X stainless steel 303, viton-o-ring, stainless steel spring

9. **Pseudocumene Rotameter** *(R1 in Figure 1)*

Make: Schutte and Koerting
Type: 'Lo-Flo' rotameter, series 1875-V outlet valve
Tube No.: 1/8 - 15 - G - 5
Float No.: BJ - 4, stainless steel
Scale: 5 inches
Capacity: 1460 cc/min air at 70°F and 14.7 psia
10. **Ammonia Rotameter** (R3 in Figure 3)

Make: Schutte and Koerting
Type: 'Lo-Flo' rotameter, series 1875-V outlet valve
Tube No.: 1/4 - 20 - G - 5
Float No.: BJ - 8, stainless steel
Scale: 5 inches
Capacity: 25,300 cc/min air at 70°F and 14.7 psia

11. **Selector Switch**

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

12. **Electrical Heating Units**

Make: Lindberg
Type: Heavy semi-cylindrical units for 1000°C

<table>
<thead>
<tr>
<th>Duty</th>
<th>Model</th>
<th>Diameter</th>
<th>Length</th>
<th>Watts*</th>
<th>Connection</th>
</tr>
</thead>
<tbody>
<tr>
<td>preheater</td>
<td>50231</td>
<td>2-3/8&quot;</td>
<td>12&quot;</td>
<td>1400</td>
<td>parallel</td>
</tr>
<tr>
<td>carburetor</td>
<td>50221</td>
<td>2-3/8&quot;</td>
<td>18&quot;</td>
<td>1000</td>
<td>parallel</td>
</tr>
<tr>
<td>reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>top</td>
<td>50301</td>
<td>3&quot;</td>
<td>3-1/2&quot;</td>
<td>600</td>
<td>series</td>
</tr>
<tr>
<td>middle</td>
<td>50311</td>
<td>3&quot;</td>
<td>5&quot;</td>
<td>850</td>
<td>parallel</td>
</tr>
<tr>
<td>bottom</td>
<td>50301</td>
<td>3&quot;</td>
<td>3-1/2&quot;</td>
<td>600</td>
<td>series</td>
</tr>
</tbody>
</table>

* 2 pieces at 115 volts
13. **Variable Transformers**

<table>
<thead>
<tr>
<th>Duty</th>
<th>Make</th>
<th>Type</th>
<th>Amps</th>
<th>Requirement at 115 Volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>preheater</td>
<td>General Radio</td>
<td>W5MMB</td>
<td>40</td>
<td>12.2</td>
</tr>
<tr>
<td>carburetor</td>
<td>Powerstat</td>
<td>116B</td>
<td>10</td>
<td>8.7</td>
</tr>
<tr>
<td>reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>top</td>
<td>Powerstat</td>
<td>116</td>
<td>8</td>
<td>5.2</td>
</tr>
<tr>
<td>middle</td>
<td>Powerstat</td>
<td>116B</td>
<td>10</td>
<td>7.4</td>
</tr>
<tr>
<td>bottom</td>
<td>Powerstat</td>
<td>116</td>
<td>8</td>
<td>5.2</td>
</tr>
<tr>
<td>heating tapes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>preheater to carburetor</td>
<td>Powerstat</td>
<td>116</td>
<td>8</td>
<td>3.5</td>
</tr>
<tr>
<td>carburetor to reactor</td>
<td>General Radio</td>
<td>W5MT</td>
<td>5</td>
<td>1.0</td>
</tr>
<tr>
<td>reactor to condenser</td>
<td>General Radio</td>
<td>W5MT</td>
<td>5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

14. **Thermocouples (TC1, TC2, TC5, TC6, TC7, TC9)**

Make: Thermocouple Products

Type: Chromel-alumel, series 400, 1/16" O.D.

Junction: W4- ungrounded

15. **Thermocouples (TC3, TC4, TC8)**

Make: Thermoelectric (Canada) Ltd.

Type: ISA-K, Chromel-alumel, 5K1100A, stainless steel 304 sheath, 1/25" O.D.

Junction: ungrounded
APPENDIX V

Determination of the Critical Diameter of the Reactor
Determination of the Critical Diameter of the Reactor

Stable Reactor Design Procedure (36)

The relevant operating conditions and system properties are:

\[ T_0 = T_j = 440^\circ C \]
\[ G = 200 \text{ lbs/sq.ft. hr.} \]
\[ \text{Rep} = 124 \]
\[ D_p = 0.0208 \text{ ft.} \]
\[ h = 43 \text{ BTU/hr. sq.ft. } ^\circ F \]
\[ \text{Ker} = 0.30 \text{ BTU/hr. sq.ft. } ^\circ F \]
\[ \gamma_0 = 0.02 \]
\[ \text{Mol.Wt.} = 106 \]
\[ C_p = 0.60 \text{ BTU/lb. } ^\circ F \]
\[ (-\Delta H) = 534,750 \text{ BTU/lb. Mole} \]
\[ E = 20,000 \text{ BTU/lb. Mole} \]
\[ \rho_F = 0.04 \text{ lbs.cu.ft.} \]
\[ \varepsilon = 0.66 \]
\[ \text{Per} = \frac{D_p C_p G}{\text{Ker}} \]
\[ = \frac{0.0208 \times 0.60 \times 200}{0.30} \]
\[ = 10.9 \]
\[ \gamma = \frac{E}{R' T_j^2} \]
\[ = \frac{20,000}{1.987 \times 820 \times 820} \]
\[ = 0.0177 \]
\[ A = 22,020 \times \frac{1}{\text{sec.}} \times 3600 \text{ sec.} \times \text{hr.} \]
\[ A_P e \]
\[ = 22,020 \times 3600 \times 0.66 \times 0.04 \]
\[ = 2,092,752 \]
\[ \gamma T_j \]
\[ = 0.0177 \times 820 \]
\[ = 13.3 \]
\[ e^{-13.3} = 0.0067 \times 0.0067 \times 0.0369 \]
\[ A_P e e^{-13.3} = 6.7 \times 6.7 \times 2.092 \times 0.0369 \]
\[ = 3.48 \]
\[ S = -\Delta H \gamma y_0 / \gamma_p \]
\[ = 534,750 \times 0.0177 \times 0.02 / 0.60 \times 106 \]
\[ = 3.0 \]
\[ L = \frac{D_p A' f_v \exp (\gamma T_i \epsilon)}{G} \]
\[ = \frac{3600 \times 22,020 \times 0.0208 \times 0.04 \times e^{-0.0177 \times 820 \times 0.66}}{200} \]
\[ = 18 \times 18.32 \times e^{-9.6} \]
\[ = 329.76 \times e^{-9.6} \]
\[ = 2.2 \times 10^{-2} \]

The procedure from this point is a repetitive, trial by error solution which converges. The final trial only will be presented here:

Let \( M = 7 \)

\( \text{Perm} = 7.2 \)

\( \bar{a} = 1.61 \)

\[ (1 - r_e^*) = \frac{1}{7} + \frac{-14-1}{56(7-1)} \]
\[ = 0.142 - \frac{15}{336} \]
\[ = 0.142 - 0.045 \]
\[ = 0.097 \]

\[ h' = \frac{43}{1 + 8.96(0.097)} \]
\[ = \frac{43}{1.87} \]
\[ = 23.0 \]
\[ S_t = \frac{23.0}{0.60 \times 200} = 0.192 \]

\( \left( \frac{N'}{S} \right) = \frac{0.192 \times 4 \times 100}{2.98 \times 8 \times 2.2} = \frac{76.8}{52.45} = 1.46 \]

\[ M \cdot S_t = 1.34 \]

\[ \beta = 1.0 \]

\( \left( \frac{N'}{S} \right)_a = 2.4 \)

\( \left( \frac{N'}{S} \right) = 1.49, \text{ which is close enough} \)

\[ D_t = 7 \times 0.0208 \sqrt{\frac{7.2}{10.9}} \times 12 = 0.1456 \times 12 \times \sqrt{0.661} = 1.32 \text{ inches} \]

The calculated critical diameter is 1.32 inches. The actual diameter of the original reactor was 1.5 inches. On the basis of the calculated critical diameter it was decided to insert a metal sleeve into the reactor to reduce the diameter of the reaction zone to one inch.
Symbols Used

A = pseudofrequency factor (h^{-1})
A' = modified pseudofrequency factor (h^{-1})
a = ratio of wall heat transfer area to flow area for cell
\bar{a} = mean value of a
a_s = heat transfer area per unit volume (ft^2/ft^3)
C = concentration of limiting reactant (lb mole/ft^3)
\bar{C} = concentration of limiting reactant (lb mole/ft^3)
c_p = heat capacity of gas (BTU/lb deg F)
D_p = mean particle diameter (ft)
D_t = internal diameter of tube (ft)
E = activation energy (BTU/lb mole)
G = (\Delta H) = heat of reaction (BTU/lb mole)
h = wall heat transfer coefficient (BTU/h ft^2 deg F)
h' = corrected, wall heat transfer coefficient (BTU/h ft^2 deg F)
ke = effective thermal conductivity (BTU/h ft deg F)
\mathcal{L} = \frac{D_pA'f_0e\exp(\gamma T_j)/G}{4St/(M\mathcal{L})}
\mathcal{M} = radial cell parameter
N' = \frac{4St/(M\mathcal{L})}{Pf_e}
Pe = Peclet number for mass transfer (=D_pG/f_0e)
Pe' = Peclet number for heat transfer (=D_pG/ke)
Pe_r,M = radial Peclet number for a system of cells of square cross section for a given value of M
R' = gas constant (BTU/lb mole deg R)
Re_p = Reynold's number (=D_pG/\mu)
\xi_p = dimensionless radial position
S = (-\Delta H)\gamma_0/\xi_p.
St = Stanton number (=h/c_pG)
T = temperature (deg R)
x = fractional conversion of limiting reactant
\gamma = mole fraction of limiting reactant
\alpha and \beta = reaction rate parameters
\gamma = (E/R'T_j)^2
\varepsilon = void fraction of bed
\beta_f = gas density

Subscripts

a = axial
j = jacket
m = maximum
o = at inlet conditions
r = radial

Overline

\sim = mole units
VITA AUCTORIS

1943
Born at Stonebury, St. Andrew's, Grenada, West Indies on August 12.

1951
Graduated College of Immaculate Conception, Port-of-Spain, Trinidad.

1957
Belmont Abbey School, Hereford, England.

1961

1968
Received Bachelor of Applied Science in Chemical Engineering from University of Windsor, Windsor, Ontario, Canada.

1968
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.