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Catalytic vapour phase ammoxidation of pseudocumene.

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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

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March, 1970

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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.

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Although the air oxidation and ammoxidation of pseudo-cumene 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 $450^{\circ}C$. The trimellitic anhydride was completely oxidized to carbon dioxide and water.

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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 occassions.

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.

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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

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was concentrated on the light aromatics - benzene, toluene, and the 'C$_8$' 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 'C$_9$' and 'C$_{10}$' polymethyl benzenes, together with benzene, 'C$_7$' and 'C$_8$' 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 (3).

As the amounts of higher polymethyl benzenes produced commercially grew, the unit price dropped rapidly (Appendix I, Figure 7). The price of pseudo-cumene 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 (2).

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 poly-ester 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$_7$' and 'C$_8$' compounds, as the 'C$_9$' and 'C$_{10}$' 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:

o-xylene   phthalic anhydride
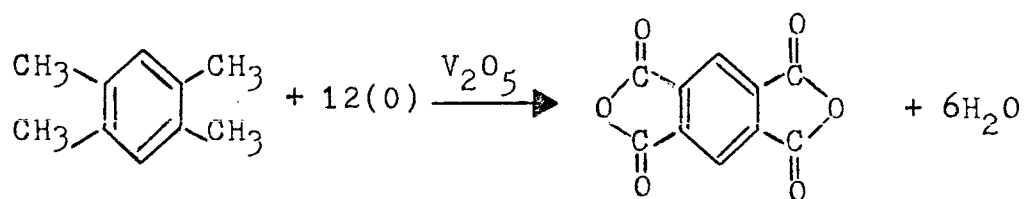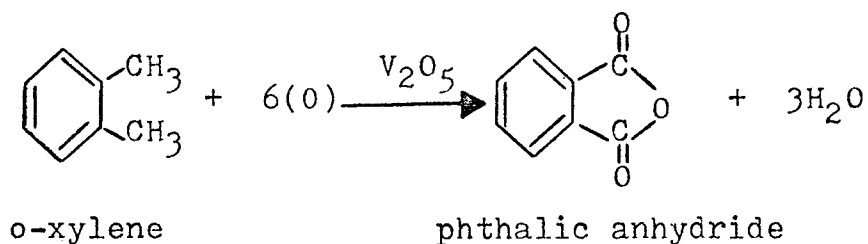
The important point to be noted is that o-xylene has one pair of methyl groups in the ortho position, and durene has two pairs of methyl groups in the ortho position. The presence of the methyl group in the ortho position appears to facilitate the vapour phase oxidation step. Pseudocumene also has a 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)

pseudocumene   trimellitic anhydride

or (ii)

pseudocumene   4-methylphthalic anhydride
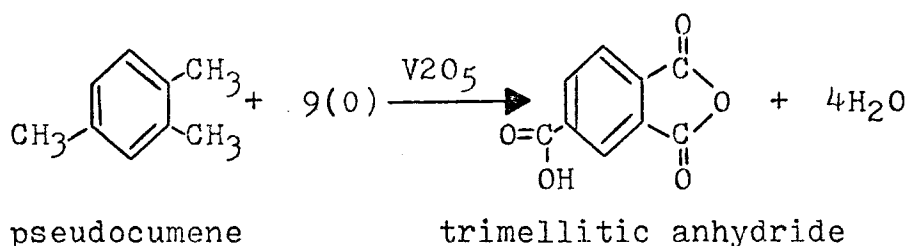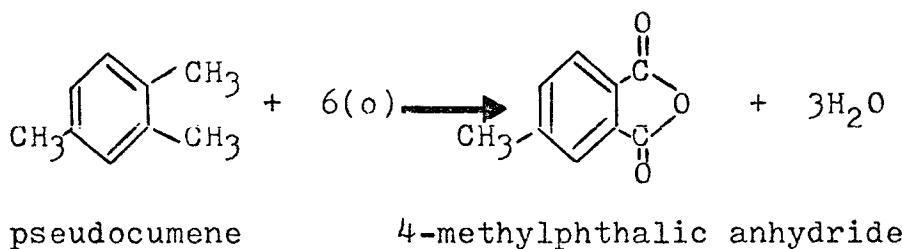
Rao (4) investigated this system and concluded that pseudocumene could not be oxidized to either of the above products in the vapour phase under the conditions which he used. His reactor, however, displayed large radial temperature profiles, which were eliminated in this study, by use of a new reactor. 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.
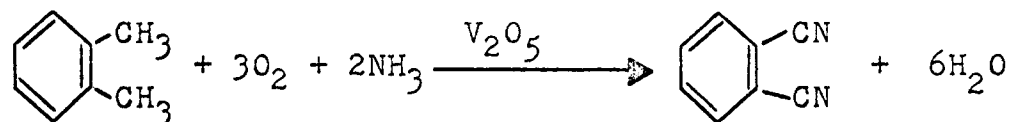
o-xylene

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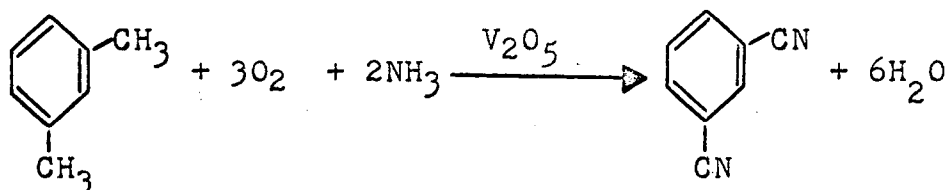
m-xylene   .   isophthalonitrile

It was expected that the ammoxidation of pseudocumene could proceed by one of the following paths.

(i)

$$\text{(dimethylbenzene)} + 3NH_3 + 4(\tfrac{1}{2}O_2) \xrightarrow{V_2O_5} \text{(tricyanobenzene)} + 9H_2O$$

1,2,4-tricyanobenzene

or (ii)

$$\text{(dimethylbenzene)} + 2NH_3 + 4(\tfrac{1}{2}O_2) \xrightarrow{V_2O_5} \text{(cyanophthalimide)}$$
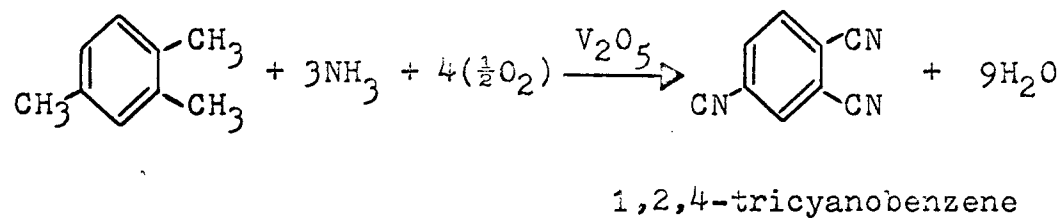
4-cyanophthalimide
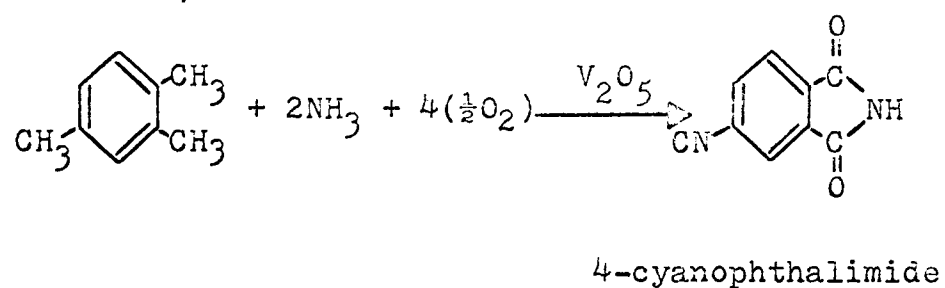
Both 1,2,4-tricyanobenzene and 4-cyano-phthalimide can easily be hydrolyzed to produce trimellitic anhydride. The objective of the project was to investigate the catalytic vapour phase ammoxidation of pseudocumene using a vanadium pentoxide on inert alumina catalyst and an air-ammonia mixture as the 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 NH_4Cl and NH_4Br. 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

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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 NH$_4$Cl. 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 perman-
ganate 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 stoicometrically 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 pseudo-
cumene. 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: O_2: NH_3
(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% V_2O_5, 5% V_2O_5 plus 9.6% K_2SO_4, 5% V_2O_5 plus 0.3% MoO_3. 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:

$$R\text{-}CH_3 \xrightarrow{O_2} RCOOH \xrightarrow{NH_3} RCOONH_4 \longrightarrow RCN.$$

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.

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CV: CHECK VALVE
NV: NEEDLE VALVE
GV: GATE VALVE
TC: THERMOCOUPLE
PR: PRESSURE REGULATOR
R : ROTAMETER
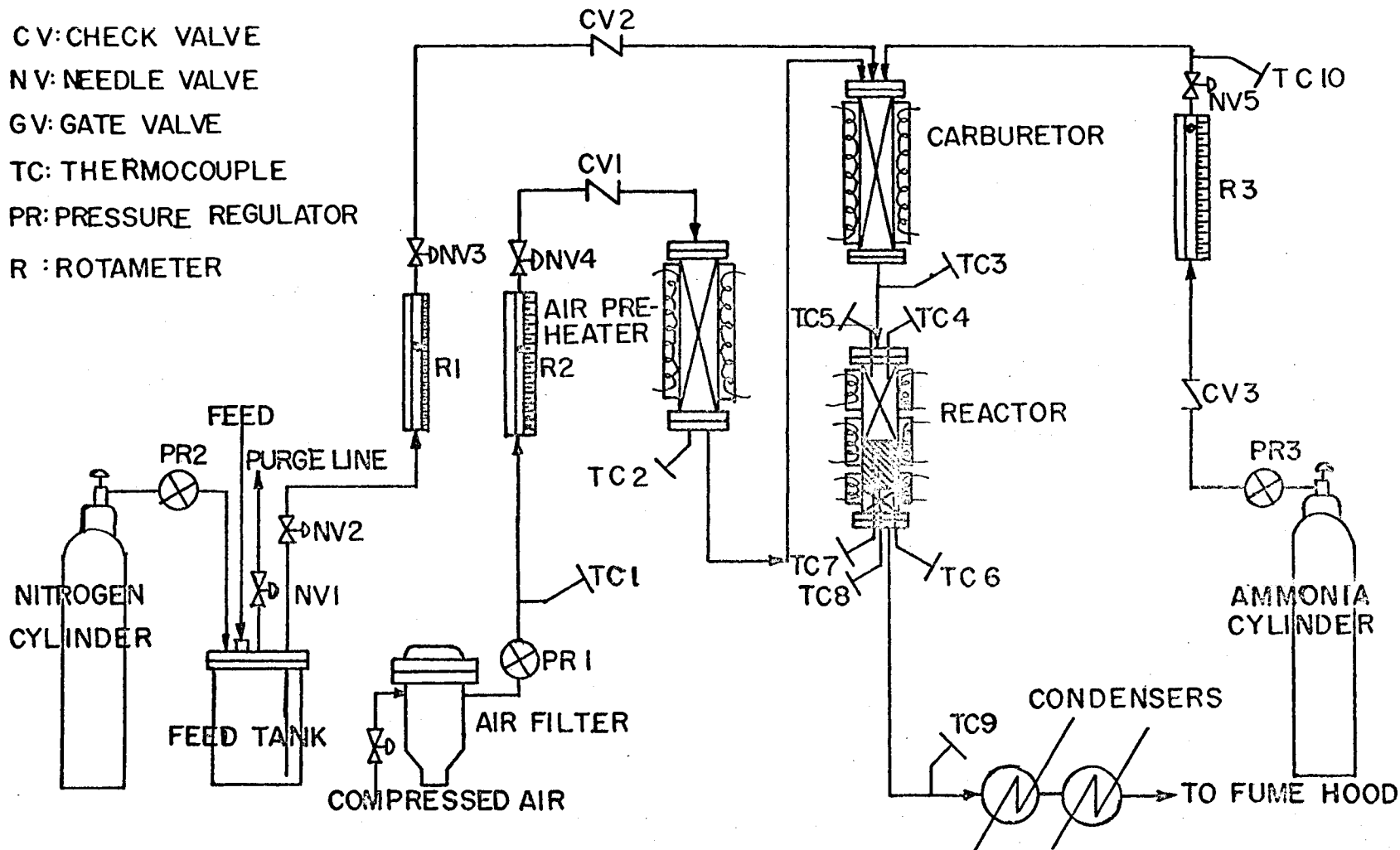
FIG.1 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS

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 14 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
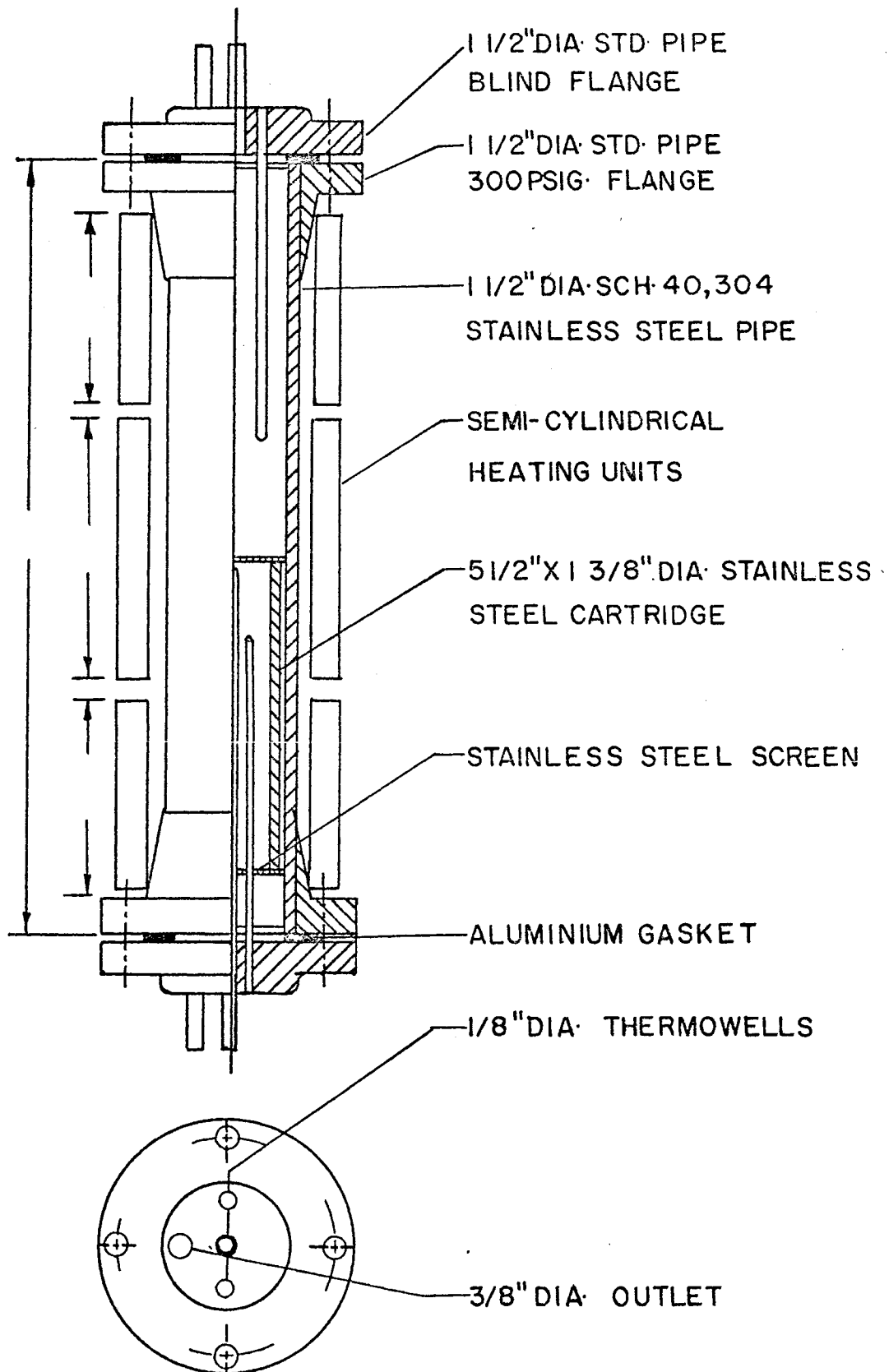
FIG. 2 SECTIONAL VIEW OF THE REACTOR

1 1/2"DIA· STD· PIPE BLIND FLANGE

1 1/2"DIA· STD· PIPE 300 PSIG· FLANGE

1 1/2"DIA·SCH· 40,304 STAINLESS STEEL PIPE

SEMI- CYLINDRICAL HEATING UNITS

5 1/2"X 1 3/8".DIA· STAINLESS STEEL CARTRIDGE

STAINLESS STEEL SCREEN

ALUMINIUM GASKET

1/8"DIA· THERMOWELLS

3/8" DIA· OUTLET

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 semi-
cylindrical heating units, connected in parallel.

I-1/2" DIA. STD. PIPE
BLIND FLANGE.

SEMICIRCULAR ELECTRIC
HEATING UNITS.

I-1/2" DIA. SCH. 40,
S. STEEL PIPE.

I-1/2" DIA. STD. PIPE
300 PSIG. FLANGE.

COPPER GASKET.

I/4" DIA. AIR INLET PORT.
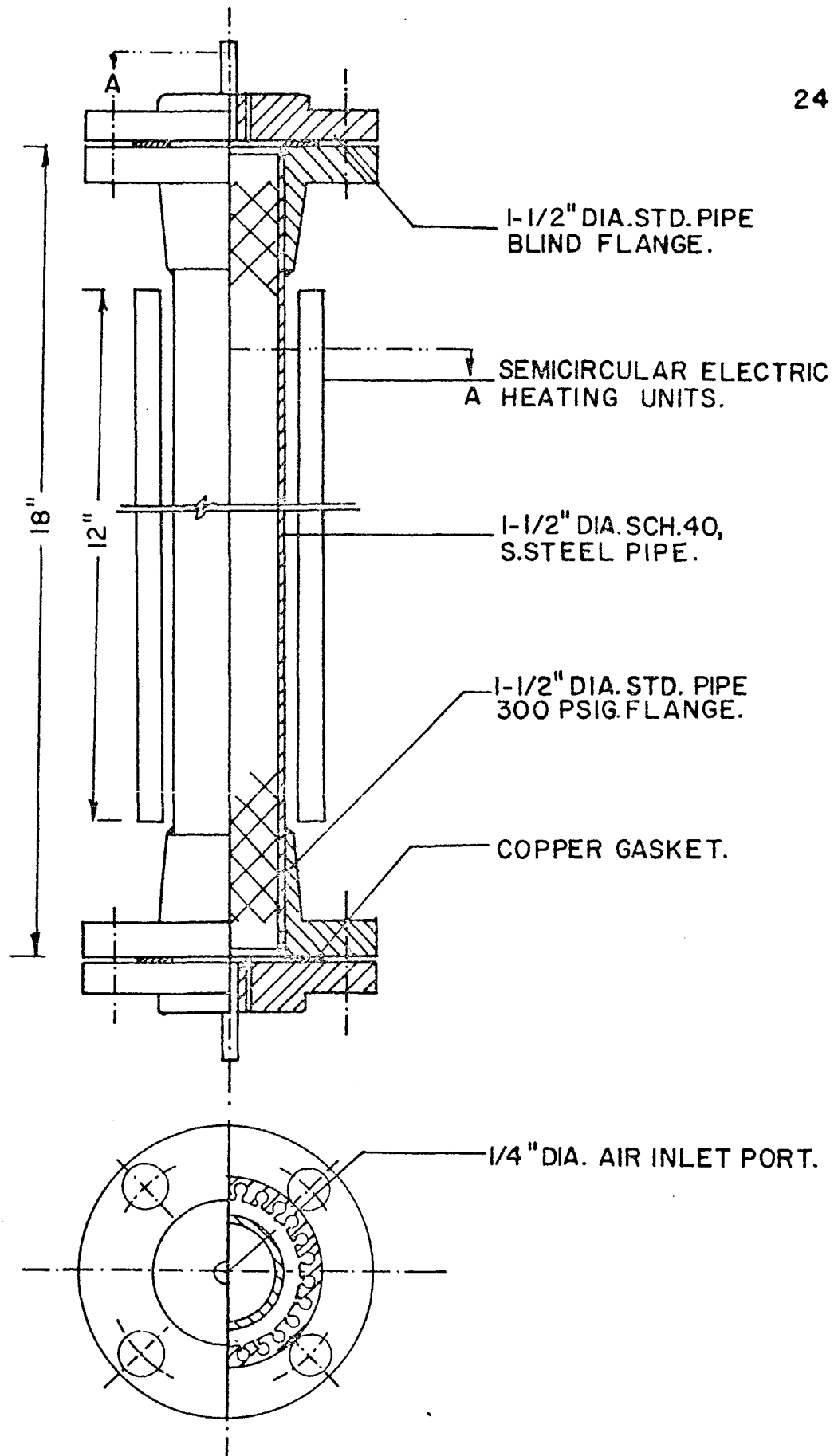
FIG. 3 SECTIONAL VIEW OF THE PREHEATER.

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

2" DIA. STD. PIPE
BLIND FLANGE.

COPPER GASKET.

2" DIA. STD. PIPE
FLANGE.

2" DIA. SCH. 40, M.S.
PIPE.

SEMICIRCULAR ELECTRIC
HEATING UNITS.

STAINLESS STEEL SCREEN.

PSEUDOCUMENE INLET
PORT.

PREHEATED AIR INLET
PORT.
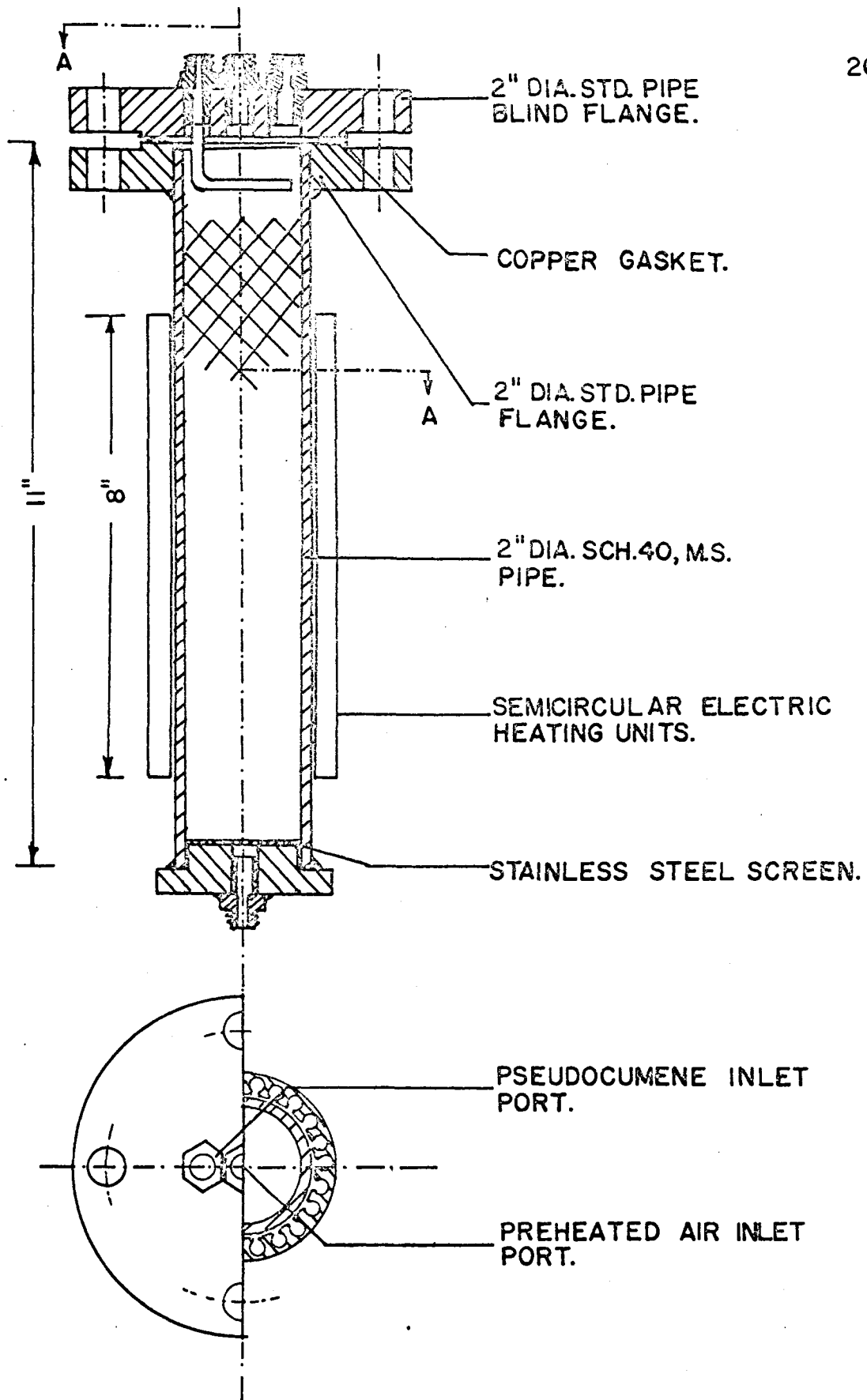
FIG. 4   SECTIONAL VIEW OF THE CARBURETOR.

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

5"DIA·STD·PIPE BLIND FLANGE

NEOPRENE GASKET

5"DIA·STD· PIPE FLANGE

5"DIA·SCH·40 MILD STEEL PIPE

PSEUDOCUMENE DISCHARGE LINE

6" DIA· MILD STEEL PLATE

1/2"DIA· PSEUDOCUMENE FEED PORT

1/4"DIA·PSEUDOCUMENE DISCHARGE

1/4"DIA· NITROGEN INLET

1/4"DIA. VENT PORT
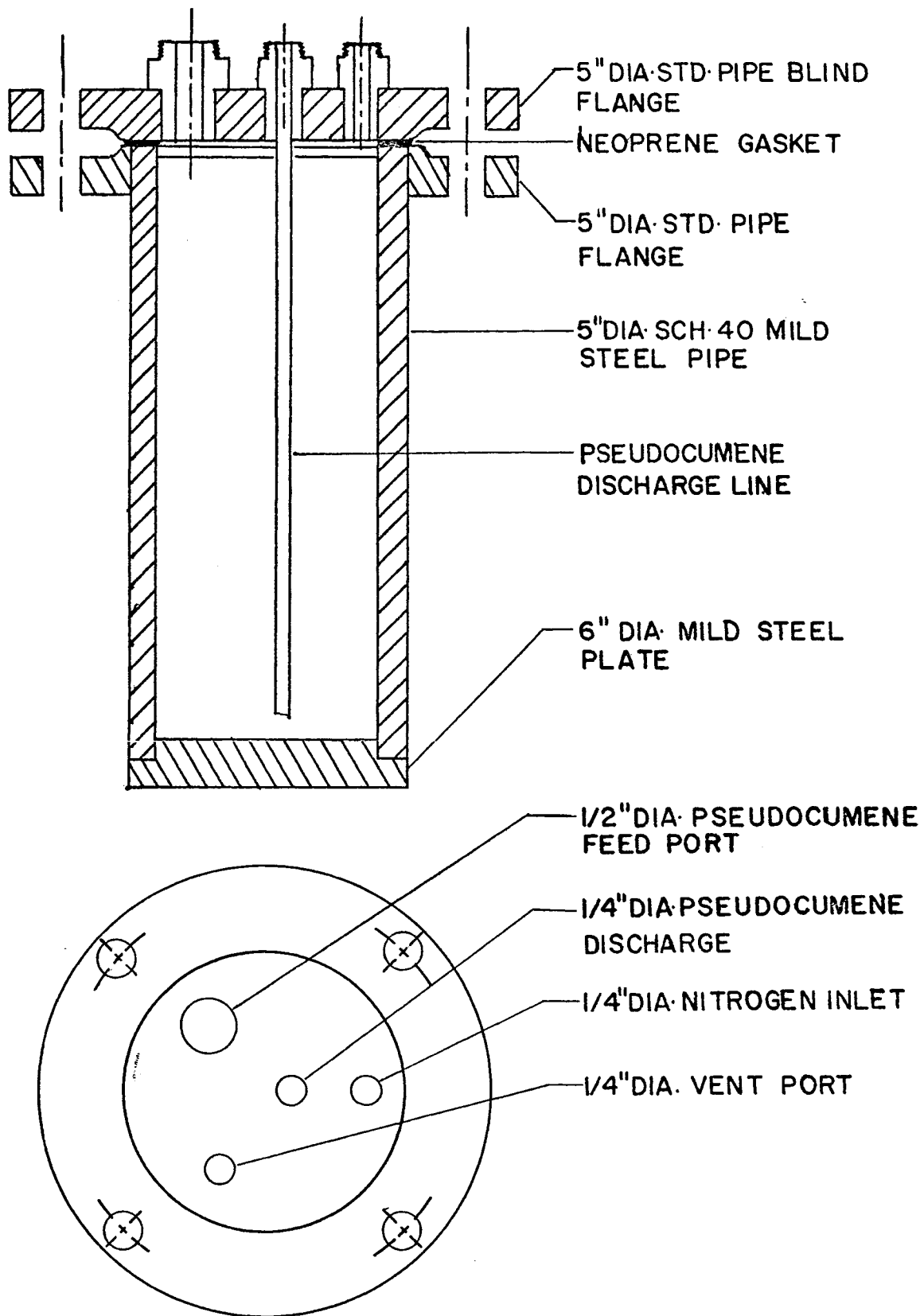
FIG. 5   SECTIONAL VIEW OF PSEUDOCUMENE FEED TANK

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. <u>Analytical Equipment</u>

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. <u>Air Oxidation of Pseudocumene</u>

A column suitable for the analysis of the aromatic anhydrides up to and including the 'C'$_9$ anhydrides could not be found. However, two columns were found which would separate the aromatic anhydrides up to and including the 'C$_8$' anhydrides. The first of these two columns was a 10 foot by 1/4 inch stainless steel column packed with 10% Bis (2-ethylhexyl tetrachlorophthalate) on 60/80 mesh, acid washed, dimethylchlorosilane 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, dimethylchlorosilane 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 pseudo-
cumene (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 tri-
mellitic 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 'C$_9$' 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, dimethylchloro-
silane treated chromosorb W could separate the aromatic
ammoxidation products up to and including the 'C$_8$'
products. The 'C$_9$' 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-tricyano-
benzene 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., $70^{\circ}C$) so that this 'standard curve' could be used to determine the flow rates for various inlet pressure conditions. Since the major components of air (N_2, O_2) 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

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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 ($\sqrt{\rho \text{ ammonia}/ \rho \text{ nitrogen}}$).
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 $\pm$ 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 thermo-
couples 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 ($0^{\circ}C$) and the melting point of pure tin
($231.85^{\circ}C$). All the thermocouples were accurate to
$\pm 0.5^{\circ}C$.

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 $400^{\circ}C$.
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 intial 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:

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(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 pseudo-
        cumene 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

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

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 pseudo-
cumene 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, 36) 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 pseudo-
cumene. 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 $350^{\circ}C$, $400^{\circ}C$, and $450^{\circ}C$ 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 $380^{\circ}C$, $400^{\circ}C$ and $420^{\circ}C$ 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 benzo-
nitrile 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

1:5:15. 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 temp-
erature 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 $280^{\circ}C$ 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 $265^{\circ}C$, 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 $285-290^{\circ}C$, sublimation occured 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 $285^{\circ}C$, 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:

pseudocumene + oxygen ————————▷ trimellitic acid

$$\xrightarrow[\text{dehydration}]{} \text{trimellitic anhydride} \xrightarrow[\text{benzene ring}]{\text{rupture of}}$$

malic acid + CO_2 + H_2O $\xrightarrow{\text{dehydration}}$

maleic anhydride

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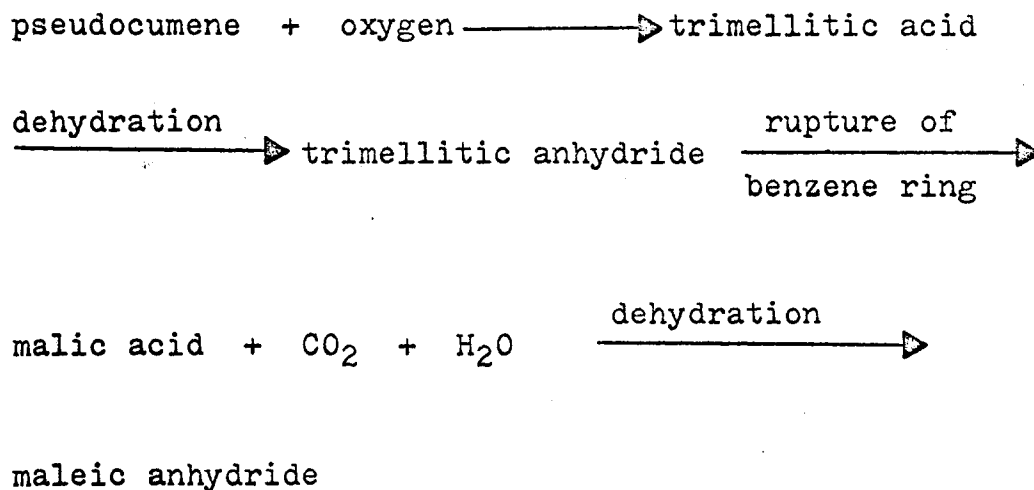
However, this scheme does not explain the absence of maleic anhydride as a product in the air oxidation of trimellitic anhydride.

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 $300^{\circ}C$. 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

1. Earhart, H.W., Lewis, T., and Schiller, J.C.,
    Commercial Newcomers: The Higher Polymethylbenzenes,
    Chem. and Engg. News, pp. 128-140, Sept. 11,(1961).

2. Haines, H.W., The Newer Aromatics, Chem. Engg.
    Progress, Vol. 59, No. 2, pp. 36-40, Feb., (1963).

3. Untapped Petrochemical Treasures, Chemical Week,
    pp. 39-44, Aug. 8, (1959).

4. Rao, S., Catalytic Vapour Phase Oxidation of Pseudo-
    cumene, M.A.Sc. Thesis, University of Windsor,
    Windsor, Ontario, (1968).

5. Backlund, P.S., (to Union Oil Co. of California),
    U.S. Patent 3,227,751, Jan. 4, (1966).

6. Backlund, P.S., (to Union Oil Co. of California),
    U.S. Patent 3,086,992, April 23, (1963).

7. Backlund, P.S., (to Union Oil Co., of California),
    U.S. Patent 3,009,953, Nov. 21, (1961).

8. Kachurina, N.Y., Prokof'er, K.V., Kazanskii, V.L.,
    and Trupanova, A.G., Trimellitic Acid Via Pseudo-
    cumene Oxidation, Neftekhimiya 5(6), pp. 880-886,
    (1965).

9. Kazanskii, V.L., Prokof'ev, K.V., Kachurina, N.Y.,
    and Trupanova, A.G., U.S.S.R. Patent 166,671, Dec.1,
    (1964).

10. Shipman, A.J., Oxidation of Organic Compounds by
    Sulphur Dioxide Under Pressure, Advance Chemistry
    Series, No. 51, pp. 52-69, Am. Chem. Soc., (1965).

11. Shipman, A.J., (to Imperial Chemical Industries
    Limited), British Patent 952,524,April 27, (1964).

12. Shipman, A.J., (to Imperial Chemical Industries
    Limited), British Patent 926,019, June 20, (1963).

13. Beilstein Organische Chemie, Band IX, System 1008, pp. 977-78, (1942).

14. Hofmann, J.E., Schrieshein, A., and Rosenfeld, D.D., Anionic Oxidation of Simple Alkyl Aromatics, Journal of the Am. Chem. Soc., 87:11, pp. 2523-24, June 5, (1965).

15. Towne, P.H., and Baldwin, R.H., Make Most Aromatic Acids Using Mid-Century Oxidation Process, Hydrocarbon Processing, Vol. 43, No. 11, pp. 149-153, (1964).

16. Burney, D.E., Weismann, G.H., and Fragan, N., Now-Dibasic Acids by Direct Oxidation, Petroleum Refiner, Vol. 38, No. 6, pp. 186, June, (1959).

17. Ibing, G.W., Industrial Processes for the Catalytic Vapour Phase Oxidation of Higher Alkylated and Condensed Aromatics to Form Polycarboxylic Acids and their Anhydrides, 7th World Petroleum Congress, Mexico, (1967).

18. Sasayama, H., Journal of the Chemical Society of Japan, Ind. Chem. Sec., (Kogyo Kagaku Zashi), Vol. 56, pp. 281, (1953).

19. Morita, S., Vapour Phase Oxidation of Methyl Naphthalenes, Bull. Chem. Soc. of Japan, Vol. 33, pp. 511, (1960).

20. Satterfield, C.N., and Loftus, J., Kinetics of the Homogeneous Partial Oxidation of o-xylene by Air, I and EC Progress Design and Development, Vol. 4, No. 1, pp. 102-105, Jan. (1965).

21. Loftus, J., and Satterfield, C.N., Mechanism of Homogeneous Gas-Phase Partial Oxidation of o-xylene, J. of Physical Chem., Vol. 69, No. 3, pp. 909-918, March, (1965).

22. Mann, R.F., and Downie, J., The Vapour-Phase Oxidation of Ortho-xylene Over a Vanadium Oxide Catalyst, The Canadian Journal of Chem. Engg., Vol. 46, pp. 71-2, Feb, (1968).

23. Satterfield, C.N., and Loftus, J., Partial Oxidation of o-xylene in Melts Containing Vanadium Pentoxide, A.I.Ch. E. Journal, Vol. 11, No, 6, pp. 1103-08, Nov. (1965).

24. Paetkau, T.R., The Partial Oxidation of o-xylene in a Transported Bed Reactor, M. Engg. Thesis, McMaster University, Hamilton, Ontario, (1966).

25. Bhattacharyya, S.K., and Krishnamurthy, R., Catalytic Vapour-Phase Oxidation of Xylenes in Fluidized Beds, J. Appl. Chem., 13, pp. 547-552, Dec, (1963).

26. Bhattacharyya, S.K., and Ganguly, N.D., Catalytic Vapour-Phase Oxidation of Organic Compounds in the Fixed as well as in Fluidized Beds, J. Indian Chem. Soc., Vol. 38, No. 8, pp. 463-80, (1961).

27. Guccione, E., New Fixed-Bed Process for Phthalic Thrives on o-xylene Feedstock, Chem. Engg. pp.132-34, June 7, (1965).

28. Forbath, T.P., Phthalic Process Makes o-xylene Look Even Better, Chem. Engg., pp. 98-100, Sept. 17, (1962).

29. Miller, R.J., (to California Research Corp.), U.S. Patent 2,576,625, Nov. 27, (1951).

30. Miller, R.J., (to California Research Corp.), U.S. Patent 2,625,555, Jan. 13, (1953).

31. Beach, L.K., (to Standard Oil, Delaware), U.S. Patent 2,509,855, May 30, (1950).

32. Ogata, Y., and Sakanishi, K., Ammoxidation of o-xylene, Chem. and Ind., pp. 2055-56, Dec. 3, (1966).

33. Taijiro, O., How to Make Xylene Diamine From Xylenes, Hydrocarbon Processes, Vol. 45, No. 11, pp. 174-5, Nov., (1966).

34. Ito, M., and Sano, K., The Kinetics of the Vapour-Phase Ammoxidation of Xylene Isomers Over a Vanadium Catalyst, Bulletin. Chem. Soc. Japan, Vol. 40, No. 6, pp. 1315-21, June (1967).

35. Hadley, D.J., The Ammoxidation Route to Nitriles, Chem. and Ind., pp. 238-243, Feb. 25, (1961).

36. Agnew, J.B., and Potter, O.E., The Design of Stable Packed Tubular Reactors for Highly Exothermic Reactions, Trans. Instn Chem. Engrs, Vol. 44, pp. T216-T222,1966.

APPENDIX I

Pseudocumene Data

Physical Properties of the Catalyst

A

1. Type   Vanadia oxidation Catalyst
                                     V-0501   S- 0.25 inch

2. V_2O_5 Content   10 %

3. Apparent Bulk Density   80 lbs/cu ft

4. Surface Area   1.0 sq m/gm

5. Size   0.25 in. spheres

B

1. Type   molybdenum trioxide

2. MoO_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, $^{\circ}$F	-47
4.	Flash point (ASTM - TCC) $^{\circ}$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)	

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 %
16.	Distillation loss	0.5%

Summary of Results of Oxidation of Pseudocumene

Catalyst (gm)	Temp. (°F)	Molar Oxygen to H.C. Ratio	Solid Deposit	Liquid Condensate
vanadium pentoxide (50 gm)	350	30 : 1	none	one phase - light yellow; G.C. analysis: pseudocumene
	370	30 : 1	none	
vanadium pentoxide (50 gm)	390	30 : 1	none	two layers: 90% light yellow top layer; 10% light brown bottom layer. G.C. analysis: top layer pseudocumene; bottom layer: maleic anhydride, water & pseudocumene. As temperature increases both the top and the bottom layers become darker in colour. The G.C. analysis yields the same qualitative results.
	400	30 :11	none	
	410	30 : 1	none	
	430	30 : 1	none	
	450	30 : 1	none	

Table 3:   Summary of Observations of Air Oxidation of Pseudocumene

Catalyst (gram)	Temp. (°F)	Molar H.C.:O$_2$:NH$_3$ Ratio	Solid Deposit	Liquid Condensate
vanadium pentoxide (50 gm)	350	1:5:15	none	one layer, light yellow in colour. G.C. analysis: pseudocumene. No reaction
		1:5:20	none	
		1:5:25	none	
vanadium pentoxide (50 gm)	400	1:5:15	none	two layers, 80% yellow bottom layer; 20% top brown layer. G.C. analysis: bottom layer:pseudocumene; top layer: maleic imide,pseudocumene & water.
		1:5:20	none	same as above,except colours of both layers lighter
		1:5:25	none	same as above,except colours of both layers lighter
vanadium pentoxide (50 gm)	450	1:5:15	none	two layers:70-80% dark yellow bottom layer; 20-30% dark brown top layer. G.C. analysis:bottom: pseudocumene;top: maleic imide,pseudo-cumene & water.
		1:5:20	none	same as above,except colours of both layers lighter
		1:5:25	none	

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

Catalyst (grams)	Temp. (°F)	Molar H.C.:O_2:NH_3 Ratio	Solid Deposit	Liquid Condensate
MoO_3 (50 gm)	350	1:5:20	none	two layers: 98% light yellow bottom layer; 2% light brown top layer. G.C. analysis: bottom: pseudocumene;top: maleic imide,water & pseudocumene
MoO_3 (50 gm)	400	1:5:20	none	two layers: 98% light yellow bottom layer; 2% light brown top layer. G.C. analysis: bottom: pseudocumene;top: maleic imide,water, & pseudocumene
MoO_3 (50 gm)	450	1:5:20	none	two layers: 98% light yellow bottom layer; 2% brown top layer. G.C. analysis: Bottom:pseudocumene; top: maleic imide, water, & pseudocumene

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

APPENDIX III

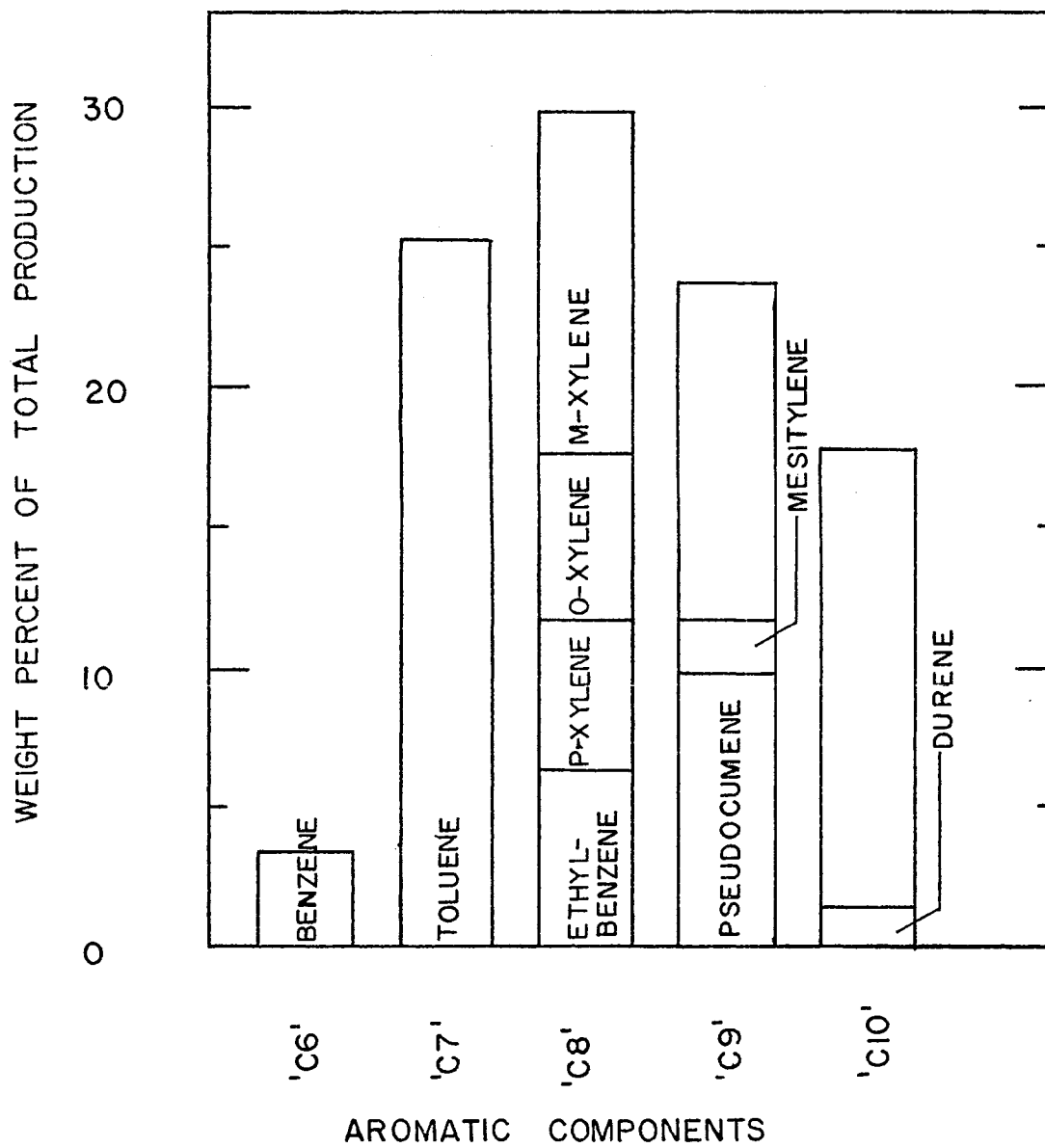Calibration Curves for the Rotameters

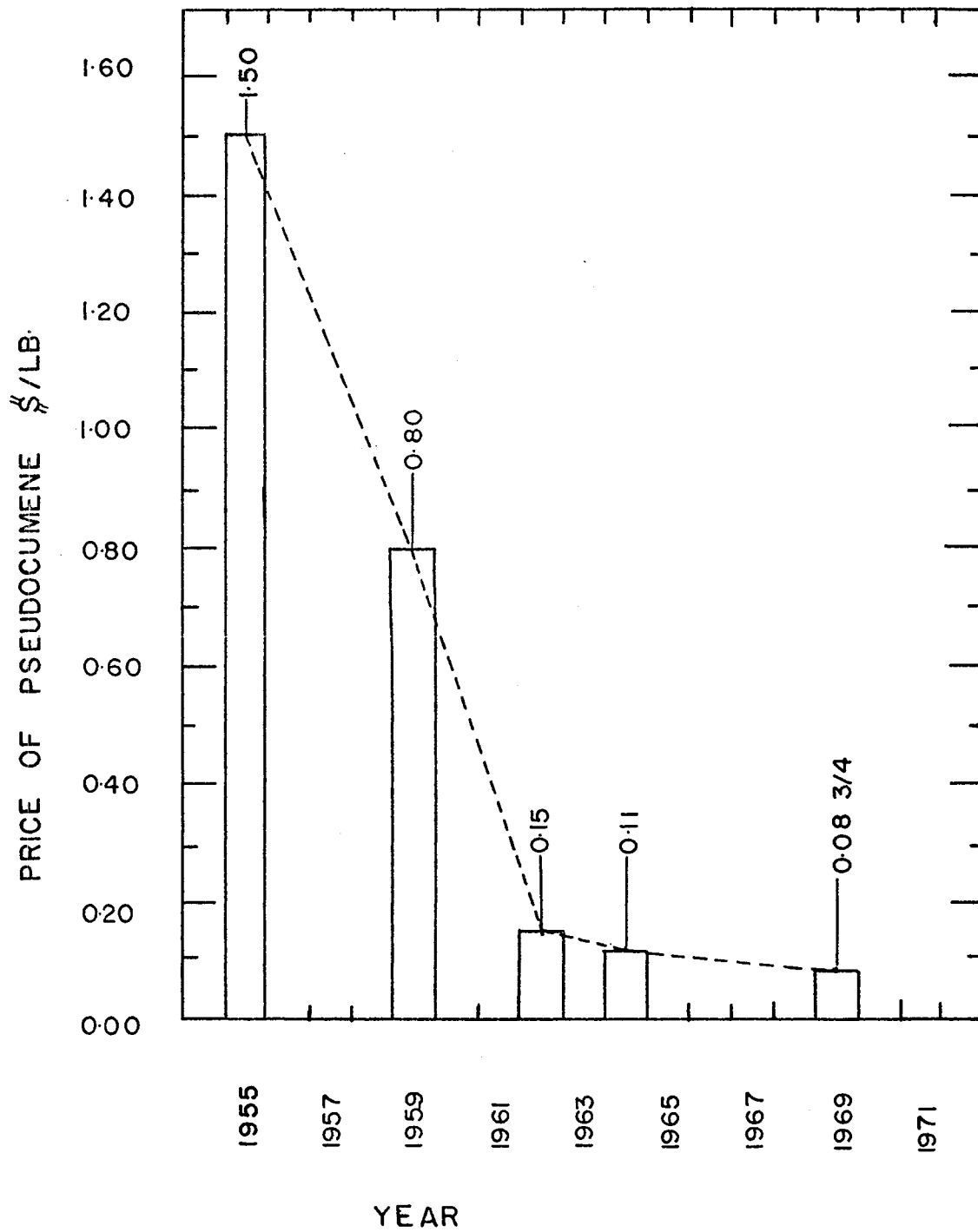FIG. 6   AROMATIC PRODUCTS FROM A GULF COAST (U·S·A·) REFINERY

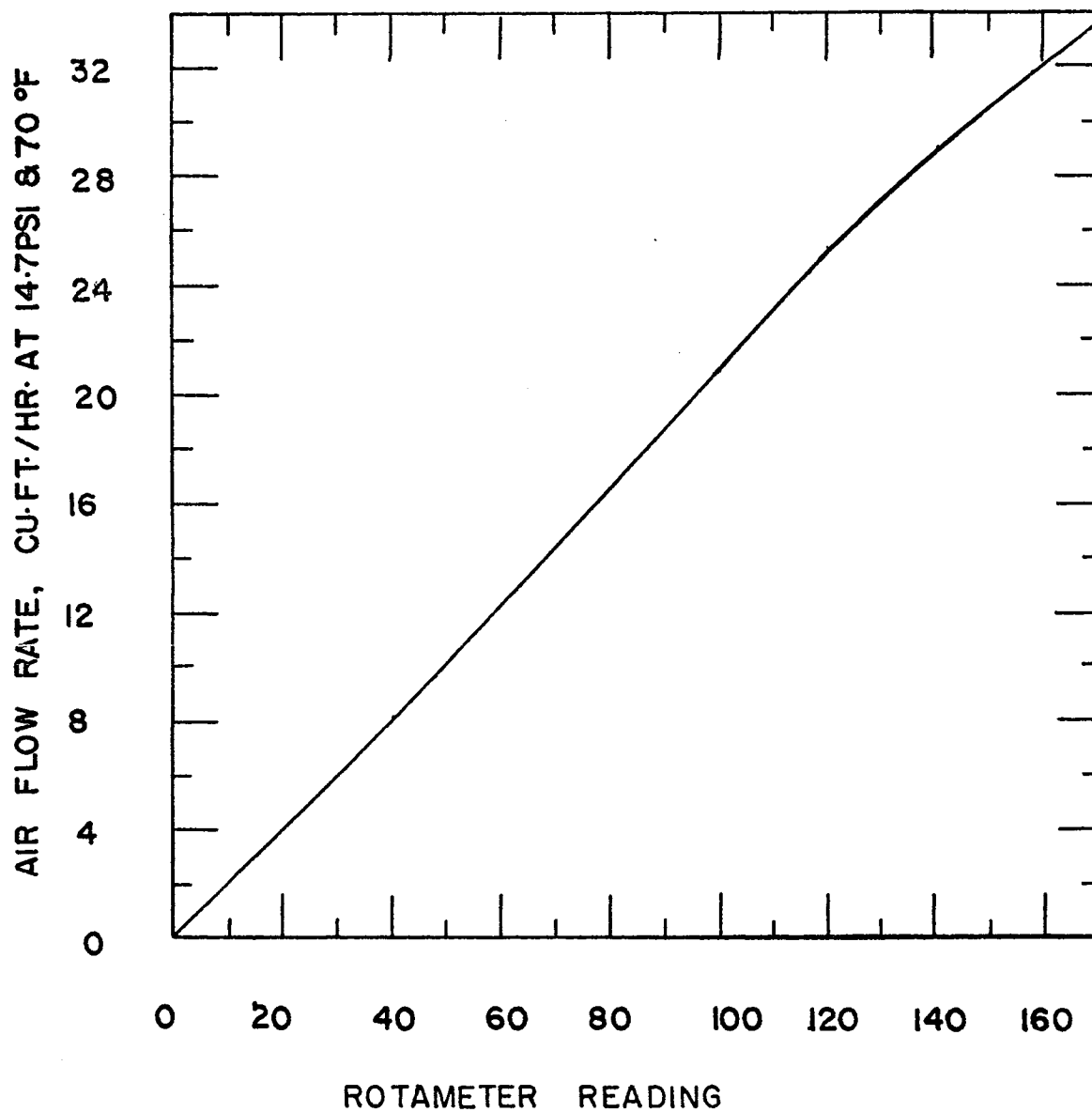FIG. 7   PRICE   VARIATION   OF   PSEUDOCUMENE

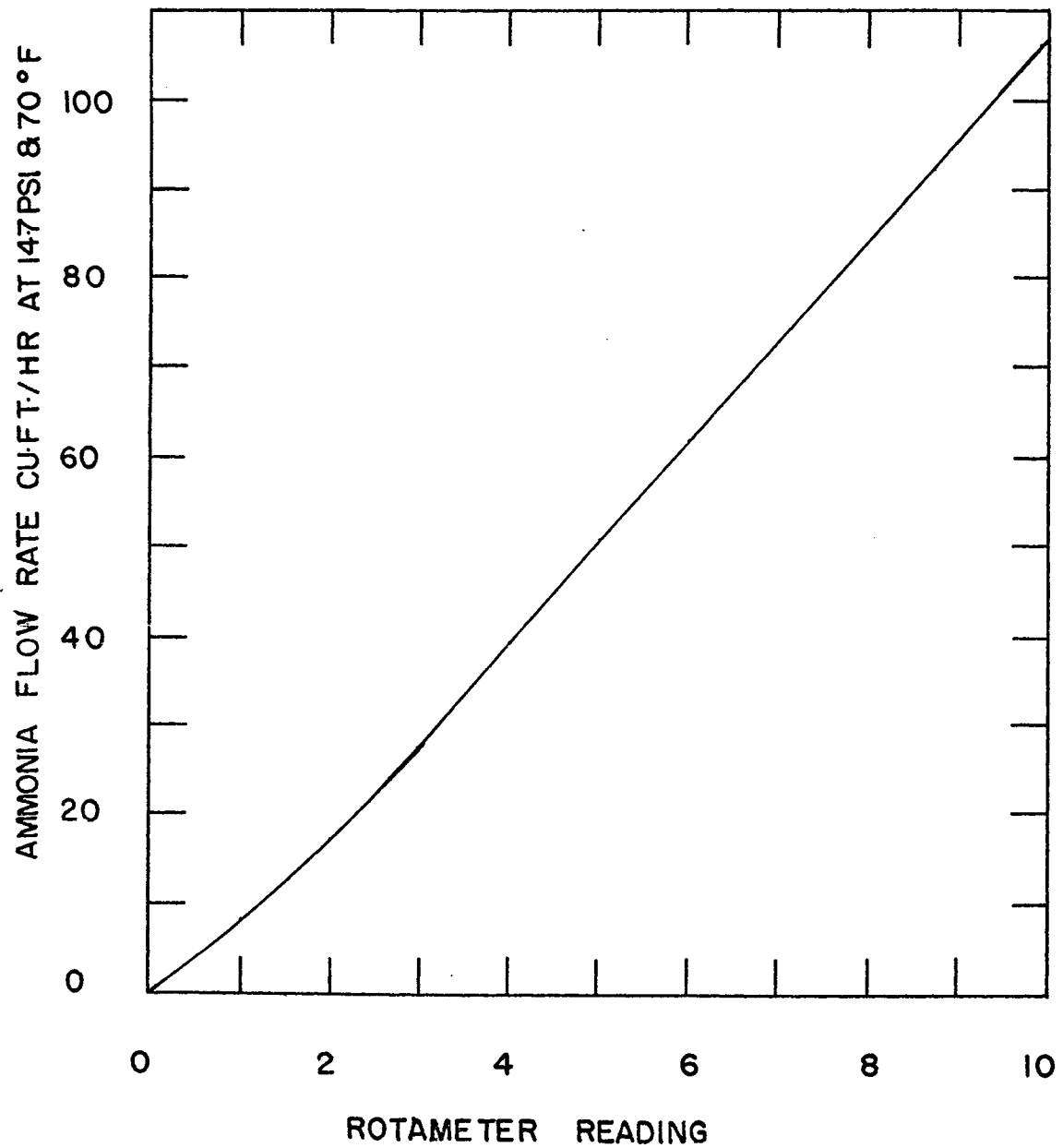Fig.8: CALIBRATION CURVE FOR AIR ROTAMETER

Fig. 9: CALIBRATION CURVE FOR AMMONIA ROTAMETER
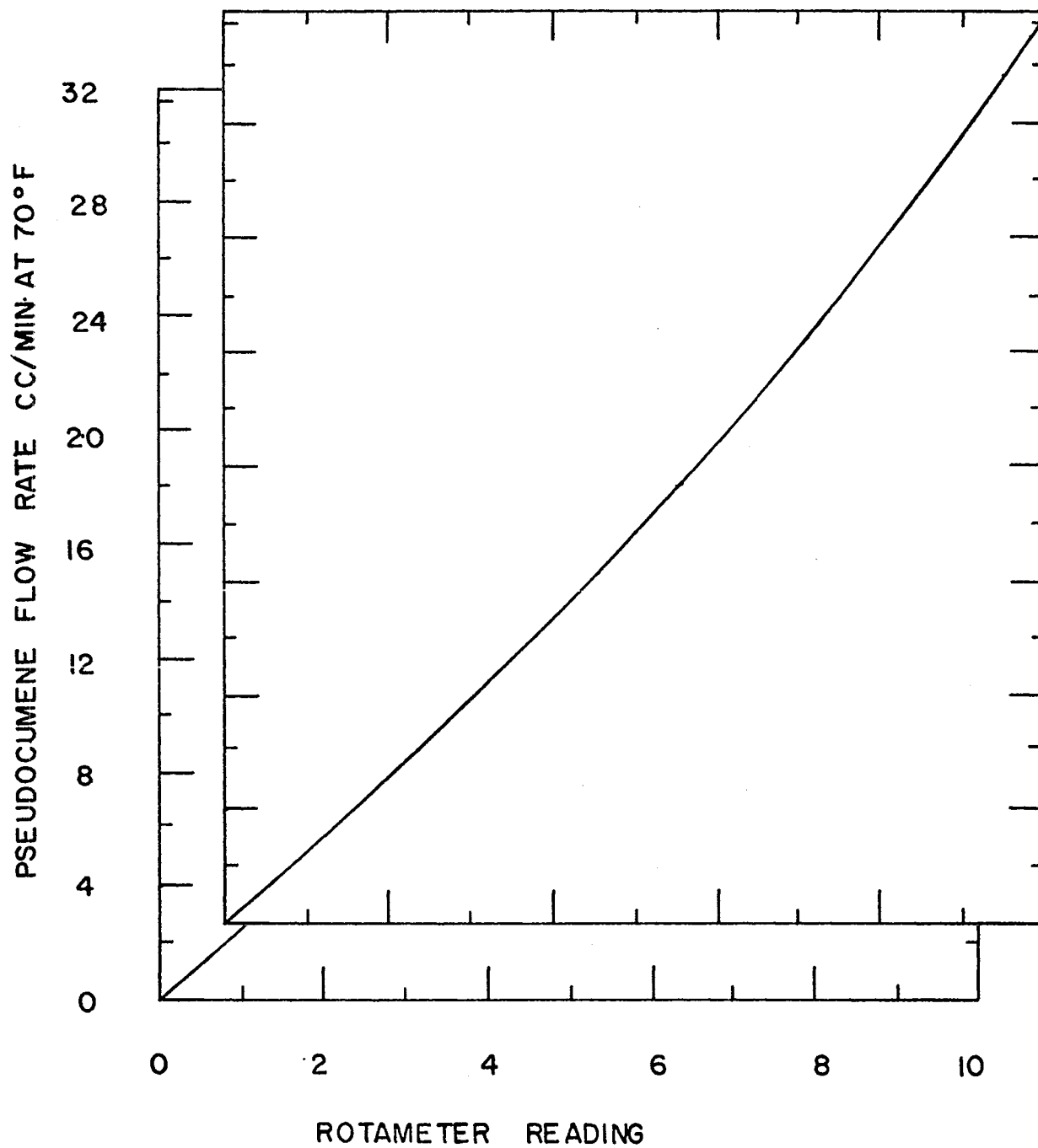
Fig. 10: CALIBRATION CURVE FOR PSEUDOCUMENE ROTAMETER

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

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4. <u>Low Pressure Regulator</u> (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. <u>Air Rotameter</u> (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. <u>Air Rotameter</u> (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. <u>Air Control Valve</u> (NV4 in Figure 1)

    Make: Matheson of Canada Ltd.

    Type: Model No. 940B (Instrument type metering valve)

    Body: Brass

    Packing: Buna - N

8. <u>Check Valves</u> (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. <u>Pseudocumene Rotameter</u> (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

Duty	Model	Diameter	Length	Watts[*]	Connection
preheater	50231	2-3/8"	12"	1400	parallel
carburetor	50221	2-3/8"	18"	1000	parallel
reactor					
top	50301	3"	3-1/2"	600	series
middle	50311	3"	5"	850	parallel
bottom	50301	3"	3-1/2"	600	series

* 2 pieces at 115 volts

13. <u>Variable Transformers</u>

Duty	Make	Type	Amps	Requirement at 115 Volts
preheater	General Radio	W5MMB	40	12.2
carburetor	Powerstat	116B	10	8.7
reactor				
top	Powerstat	116	8	5.2
middle	Powerstat	116B	10	7.4
bottom	Powerstat	116	8	5.2
heating tapes				
preheater to carburetor	Powerstat	116	8	3.5
carburetor to reactor	General Radio	W5MT	5	1.0
reactor to condenser	General Radio	W5MT	5	1.0

14. <u>Thermocouples</u> (TC1, TC2, TC5, TC6, TC7, TC9)

Make: Thermocouple Products

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

Junction: W4- ungrounded

15. <u>Thermocouples</u> (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_o	=	T_j	=	440^oC
G	=	200 lbs/sq.ft. hr.		
Rep	=	124		
D_p	=	0.0208 ft.		
h	=	43 BTU/hr. sq.ft. ^oF		
Ker	=	0.30 BTU/hr. sq.ft. ^oF		
y_o	=	0.02		
Mol.Wt.	=	106		
C_p	=	0.60 BTU/lb.^oF		
$(-\Delta H)$	=	534,750 BTU/lb. Mole		
E	=	20,000 BTU/lb. Mole		
ρ_F	=	0.04 lbs.cu.ft.		
ε	=	0.66		

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$$P\acute{e}r = \frac{D_p \ C_p \ G}{Ker}$$

$$= \frac{0.0208 \times 0.60 \times 200}{0.30}$$

$$= 10.9$$

$$\gamma = \frac{E}{R' \ T_j^2}$$

$$= \frac{20,000}{1.987 \times 820 \times 820}$$

$$= 0.0177$$

$$A = 22,020 \ \frac{1}{sec.} \times 3600 \ \frac{sec.}{hr.}$$

$$A\widetilde{\rho}_{f_o}e = 22,020 \times 3600 \times 0.66 \times 0.04$$

$$= 2,092,752$$

$$\gamma T_j = 0.0177 \times 820$$

$$= 13.3$$

$$e^{-13.3} = 0.0067 \times 0.0067 \times 0.0369$$

$$A\widetilde{\rho}_{f_o}e \ e^{-13.3} = 6.7 \times 6.7 \times 2.092 \times 0.0369$$

$$= 3.48$$

$$S = -\Delta H \gamma y_o / \widetilde{C}_p$$

$$= 534,750 \times 0.0177 \times 0.02/ \ 0.60 \times 106$$

$$\cong 3.0$$

$$\mathscr{L} = \frac{D_p \, A' \rho_{fc} \exp (\gamma \, T_j \Theta)}{G}$$

$$= \frac{3600 \times 22{,}020 \times 0.0208 \times 0.04 \times e^{-0.0177 \times 820 \times 0.66}}{200}$$

$$= 18 \times 18.32 \times e^{-9.6}$$

$$= 329.76 \times e^{-9.6}$$

$$= 2.2 \times 10^{-2}$$

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

$$\text{Let} \quad M = 7$$

$$P_{er,m} = 7.2$$

$$\bar{a} = 1.61$$

$$(1 - r_e{}^*) = \frac{1}{7} + \frac{-14-1}{56(7-1)}$$

$$= 0.142 - \frac{15}{336}$$

$$= 0.142 - 0.045$$

$$= 0.097$$

$$h' = \frac{43}{1 + 8.96(0.097)}$$

$$= \frac{43}{1.87}$$

$$= 23.0$$

$$S_t = \frac{23.0}{0.60 \times 200}$$

$$= 0.192$$

$$\left(\frac{N'}{S}\right) = \frac{0.192 \times 4 \times 100}{2.98 \times 8 \times 2.2}$$

$$= \frac{76.8}{52.45}$$

$$= 1.46$$

$$M.S_t = 1.34$$

$$\beta = 1.0$$

$$\left(\frac{N'}{S}\right)\overline{a} = 2.4$$

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

$$D_t = 7 \times 0.0208 \sqrt{\frac{7.2}{10.9}} \times 12$$

$$= 0.1456 \times 12 \times \sqrt{0.661}$$

$$= 1.32 \text{ inches}$$

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_v	=	heat transfer area per unit volume (ft^2/ft^3)
C	=	concentration of limiting reactant (lb mole/$ft3$)
c_p	=	heat capacity of gas (BTU/lb degF)
D_p	=	mean particle diameter (ft)
D_t	=	internal diameter of tube (ft)
E	=	activation energy (BTU/lb mole)
G	=	mass velocity of gas (lb/ h ft^2)
$(-\Delta H)$	=	heat of reaction (BTU/ lb mole)
h	=	wall heat transfer coefficient (BTU/h ft^2deg F)
h'	=	corrected wall heat transfer coefficient (BTU/h ft^2 deg F)
k_e	=	effective thermal conductivity (BTU/h ft deg F)
$\mathcal{L}$	=	$D_p A° \rho_{fo} e \exp(\gamma T_j)/G$
M	=	radial cell parameter
N'	=	$4St/(M \cdot \mathcal{L})$
Pe	=	Peclet number for mass transfer ($=D_p G/\rho_f \mathcal{D}_e$)
Pe°	=	Peclet number for heat transfer ($=D_p c_p G/k_e$)
$Pe_{r,M}$	=	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 ($=D_p G/\mu$)
r_e^*	=	dimensionless radial position
S	=	$(-\Delta H)\gamma y_0/\tilde{c}_p$.
St	=	Stanton number ($=h/c_p G$)
T	=	temperature (deg R)
x	=	fractional conversion of limiting reactant
y	=	mole fraction of limiting reactant
α and β	=	reaction rate parameters
γ	=	$(E/R'T_j^2)$
e	=	void fraction of bed
ρ_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	City of Westminster College, London, England.
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.

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