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Vapor phase catalytic air oxidation of P-cymene

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FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

NEWARK, NEW JERSEY

JUNE, 1952

VAPOR PHASE CATALYTIC AIR OXIDATION OF P-CYMEENE

BY

SALVATORE J. FINELLI

A THESIS
SUBMITTED TO THE FACULTY OF
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VAPOR PHASE CATALYTIC AIR OXIDATION OF P-CYMENE

Introduction

After several years experience including the oxidation of toluene, p-xylene, p-chlortoluene, 2-4 dichlor-toluene, 2-6 dichlortoluene, 3-4 dichlor-toluene and B-picoline, the writer became interested in the vapor phase oxidation of p-cymene to produce aldehydes.

Literature contains information on the formation of p-toluic acid and terephthalic acid but no information is found on the conditions for aldehyde formation. There is mention that aldehyde production occurs at temperatures below 350° C at low air flow rates and with particular catalysts, but no specific information has been given. The writer therefore decided to investigate whether or not aldehyde formation does occur with vanadium catalyst and, if so, at what conditions.

In order to establish whether vanadium catalyst would oxidize p-cymene, a fluid catalyst unit was built and then tested with toluene for the formation of benzaldehyde.

The construction of the unit, preparation of the catalyst, preliminary testing of the unit and actual oxidation of p-cymene are therefore reported in successive order.

The factors which influence oxidation are as follows:

1. Oxygen to hydrocarbon ratio.
2. Catalyst form and activity rating.

3. Pressure.
4. Temperature.
5. Effect of water vapor and fixed gases.
6. Catalyst deterioration and revivification.
7. Time of contact.
8. Temperature control.
9. Secondary reactions.

The effects of all these variables could not be evaluated at this time, but it is hoped that other workers will undertake this project and contribute some knowledge to this subject.

The purpose for this work was therefore threefold: the first object was to build a catalytic vapor phase unit employing fluid catalyst so that application of fluid bed technique could be applied to another chemical reaction, the oxidation of p-cymene. The second object was to determine whether vanadium oxide catalyst would produce aldehyde formation. The third object was to obtain additional data on p-cymene oxidation in order to have some comparison with oxidation carried out in a fixed bed reactor and reported by Senseman and Stabbs (15).

MATERIALS OF CONSTRUCTION

The unit was built of 304 stainless steel, including the pre-heater line, catalyst sparging section, cyclone separator and product condenser.

A stainless steel Corson-Cervery Micro-Bellows feed pump was installed. Model N. 1000, serial 422, 110 volts, 60 cycles, capacity 30 to 2000 cc/hr. The feed reservoir was a 1,000 ml. graduated pyrex cylinder.

The gas sparging section consisted of a 2-inch standard stainless steel pipe with a 55 per cent porosity aloxite thimble type gas sparger as shown in Figure 3. This type gas diffuser, manufactured by the Corborundum Company, has proven satisfactory over a five year period. These gas spargers are to be preferred over the flat plate type gas diffusion units. It is highly recommended that thimble type spargers be used in pilot plant and commercial units since they offer better fluidization than spiders, pipe coils, orifices or flat plate spargers. Surging of the catalyst bed is minimized by use of thimble type spargers.

The unit was welded with stainless steel welding rods, and each section of the unit was tested with air pressure. The reactor section was tested at 50 psig. and the cyclone separator and sparging section were tested at 30 psig. No need for higher pressure was evident at the time of construction as the work planned for this unit would be at substantially atmospheric pressure.

The 1-inch I.D. stainless steel water cooled condenser was tested and found tight at 50 psig.

The reactor and cyclone sections were insulated with standard 2-inch and 3-inch magnesia pipe covering.

A description of the various parts of the unit as shown on Figure 1 are as follows:

DESCRIPTION OF PARTS

Reactor: This was made from a 2" standard 304 stainless steel pipe. One-half inch thick flanges were welded at each end and thermowells made of 1/8" I.D. x 1/4" O.D. stainless steel tubing inserted at 6-1/2", 12", 12" and 12" spacings from the bottom flange. These were welded to the reactor wall and were inclined 40° with the vertical axis. The overall length of the reactor was 7'-1/4".

Gas Sparger: A 9" length of the 2" pipe cut from the reactor stock material was used to build the sparging section. A flat faced flange of 5/8" thickness was available and used for this unit. The bottom of sparger was cut at a 45° angle in order to insure complete draining of the catalyst from the unit when desired. A 1/4" S.S. nipple, welded at one end, was used as a catalyst drain plug. This nipple measured 3-3/4" long in order to extend beyond the magnesia pipe insulation and also so that a wrench could be applied to the plug to tighten or remove it.

A 1/2" standard S.S. pipe was inserted into the side wall of the sparger section and welded in position. The pipe extended 10-1/2" from the center line of the pipe to the outside end. The inside portion of this pipe was curved so as to make an ell and the aloxite thimble type sparger was set on this threaded end.

Heaters: Three strip heaters, 1,000 watts each, 230 volt, Chromalox type, were strapped on to the bottom section of the reactor. These heaters measured 1-1/2" wide, 1/4" thick and 36" long. They were spaced 120° apart and wired in parallel by use of 1/8" diameter Nichrome wire. The wire was beaded and extended six inches beyond the outside insulation and was connected to the power source from the 7.5 KVA powerstat. Parker fittings were used at all wire junctions and insulation tape applied.

Cyclone Separator: The cyclone was built of 1/32" thick stainless steel plate, rolled and welded. The top section was 8" ID and the bottom section of 2" Std. 304 S.S. pipe. The overall height of the cyclone was 18-1/2". A 1/2" elbow was welded on the top for vapors to pass out into the condenser. A 1/4" O.D. S.S. thermowell, 6-3/4" long, was inserted on the top plate and welded in place. This weld extended 2-1/4" into the cyclone section. A 1/2" S.S. nipple, 4-1/2" long, was welded on the top plate. This served as a catalyst feed point. A cap was placed on the top end of this nipple. A standard 150# slip-on steel flange was welded to the bottom 2" section of the cyclone.

Flanges: Standard 150# slip-on flanges were used in the assembly of the reactor, sparger section and cyclone. 5/8" dia. bolts, 2" long, were used in the assembly.

- Gaskets: 2" I.D. x 3" O.D. durable gasket material was used.
- Product Condenser: A 1" Std. 304 S.S. pipe, 48" long, was used. The water jacket was a 2" Std. galvanized pipe 42" long. Collars, 1/2" thick, were cut and welded to each end so as to seal the water jacket. Two 1/4" nipples, 2" long, were welded 3" from each end to provide for in and out flow of water to the jacket.
- A reducing coupling was used on top of the condenser so that it would fit the 1/2" vapor line from the cyclone.
- Product Receivers: These were 2-liter, 3 neck pyrex flasks. The first receiver was equipped with a thermometer to measure the temperature of the condensate and a bottom drain valve to remove product from the receiver. A side stop-cock also permitted taking a gas sample or venting the unit if necessary.
- Product Condensers: These were pyrex glass condensers, 40" long, 1/4" ID and provided with a water jacket. Glass tubing, 3/8" ID and of proper length, was used to connect the outflow neck of the product receivers to top of the glass product condensers. The top curved loop on this tubing was 8 inches. All connections to flasks and condensers were made with rubber stoppers.
- Reactor Powerstat: A variable transformer of Type 1256 was used. This was panel-mounted and used to control the heat to the reactor.

A masonite box was set around the transformer for protection of the instrument and also as a safety measure.

Superior Electric Company of Bristol, Connecticut, manufactured this instrument.

**Feed Line
Variac:**

A small variable transformer of Type 116 connected to the bottom of the sparging section was used for control of current to the heating coil on the hydrocarbon feed line. The current was adjusted so as to maintain the hydrocarbon in a vapor state. This instrument was manufactured by the Superior Electric Company and was operated on the 110 volt circuit.

Carbon Trap: A carbon trap made from a 2" I.D. pyrex glass pipe, 3 feet long, was used to adsorb hydrocarbon vapors on granular activated carbon. The carbon was activated by steaming, drying and cooling before use. A rubber stopper was used at each end of the glass pipe to hold the carbon granules in place. Entrance into and exit from the carbon bed was by means of a 1/4" pipe nipple inserted through each stopper.

Air Rotameter:

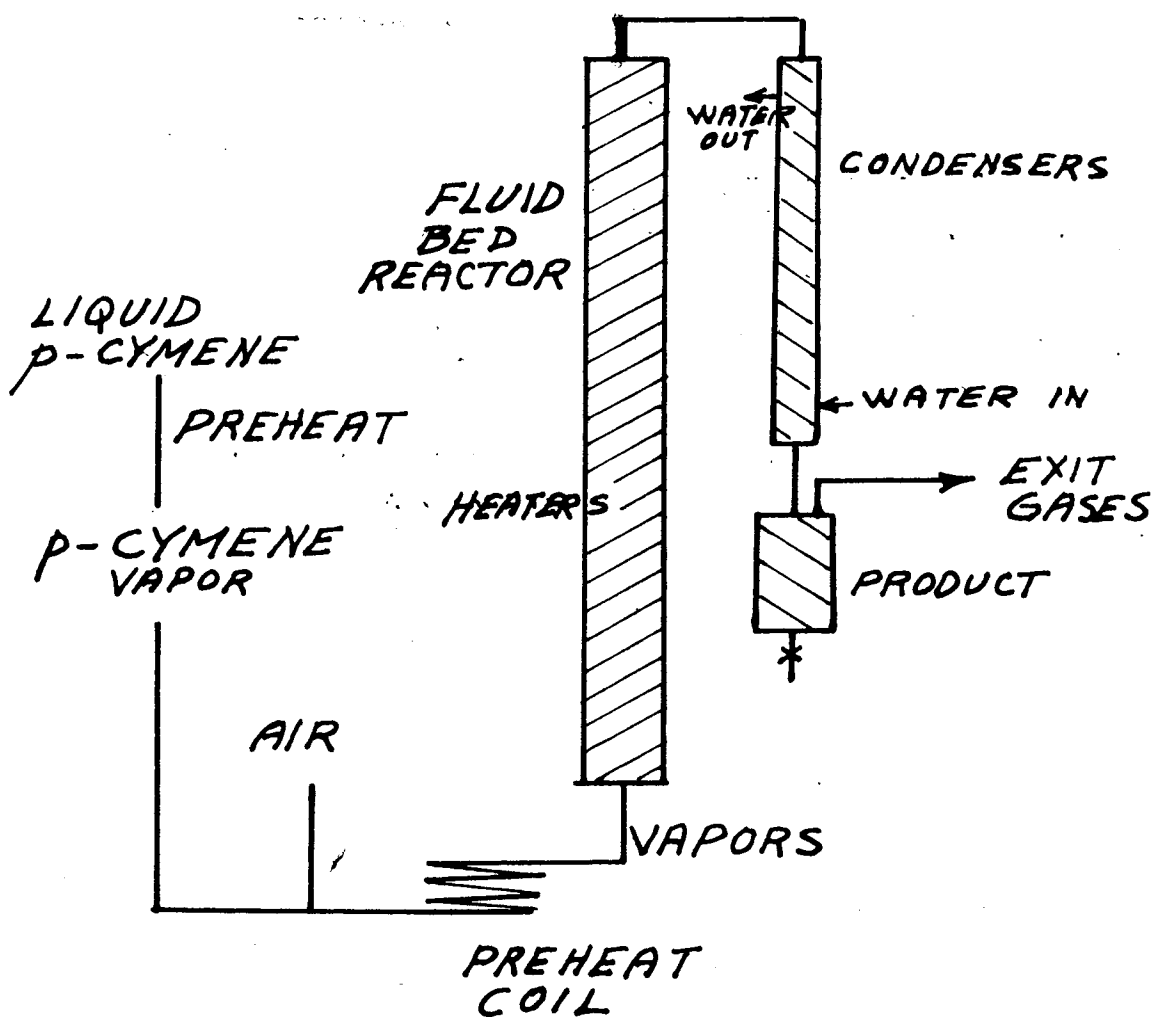
A Fischer and Porter Precision Bore Rotameter tube No. 2B-25 with a scale of 0 to 10 inches was used. This rotameter was calibrated for air flow at 15 psig. by means of a standard wet gas meter. A calibration curve was plotted and used throughout the experiments. Connections to and from the air rotameter were made by

1/4" pipe fittings.

Air Pressure Reducer: A pressure regulator manufactured by the Atlas Valve Co. of Newark, New Jersey, was used to reduce the air pressure from 75 psig. to 15 psig.

Pressure Indicating Gauge: A pressure gauge manufactured by J. P. March Corporation of Chicago was used. The scale range was 0-30 psig.

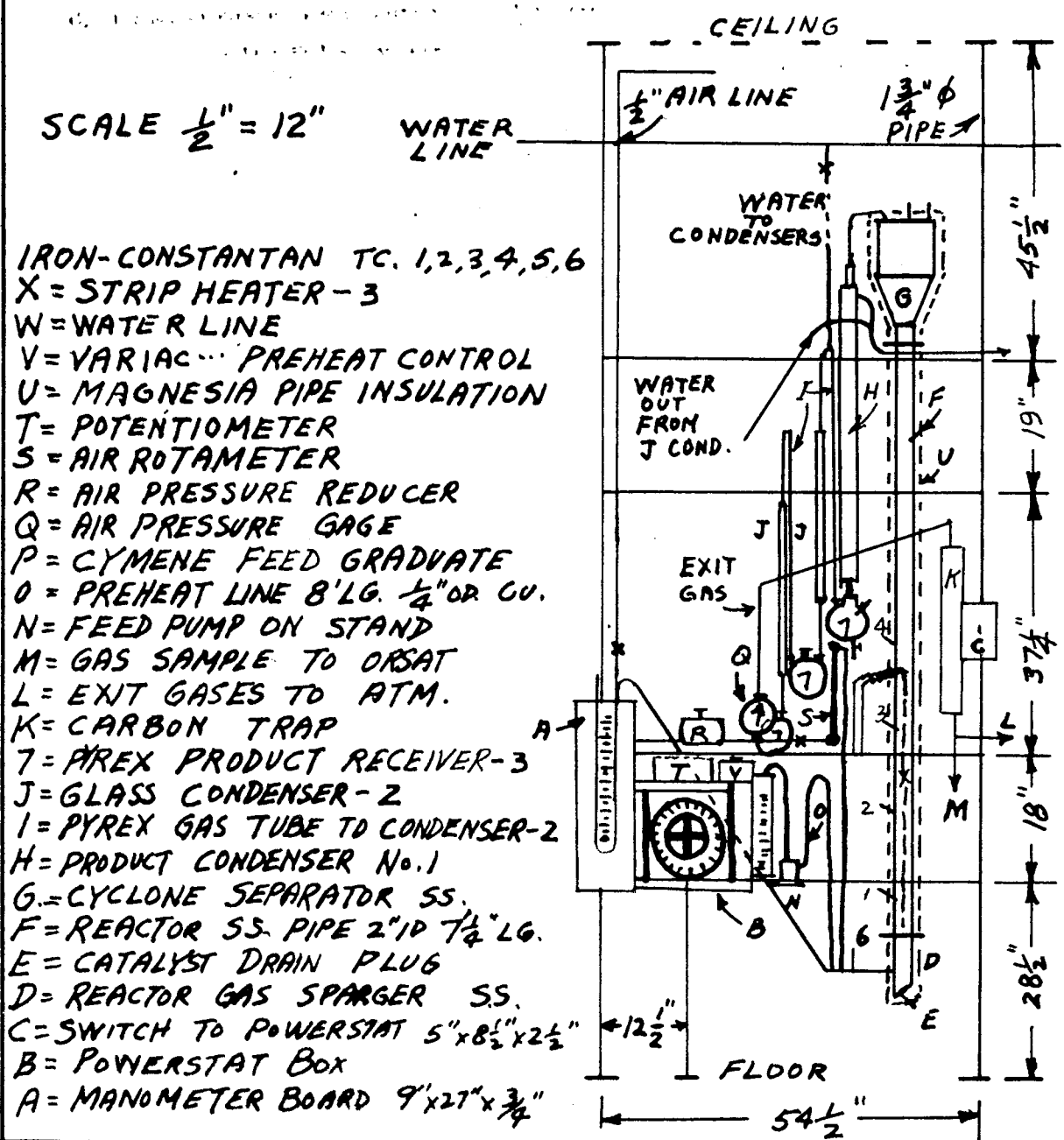
AIR OXIDATION OF P-CYMENE
FIGURE NO. 1
FLOW DIAGRAM



5/15/52 S.F.

CATALYTIC AIR OXIDATION UNIT FOR P-CYMENE

FIGURE NO. 2

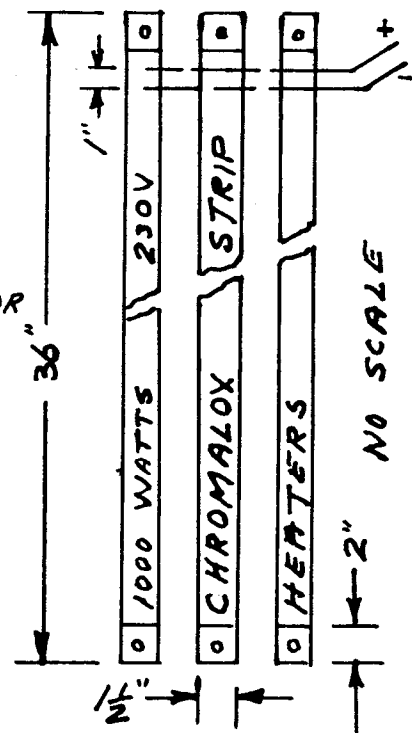
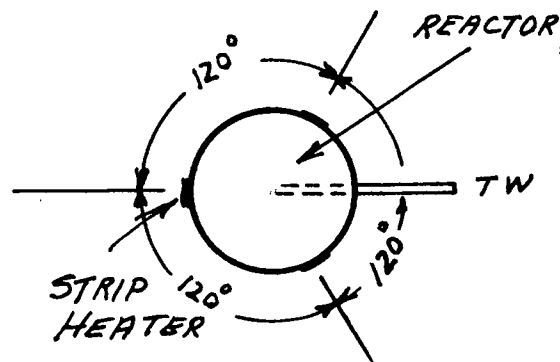
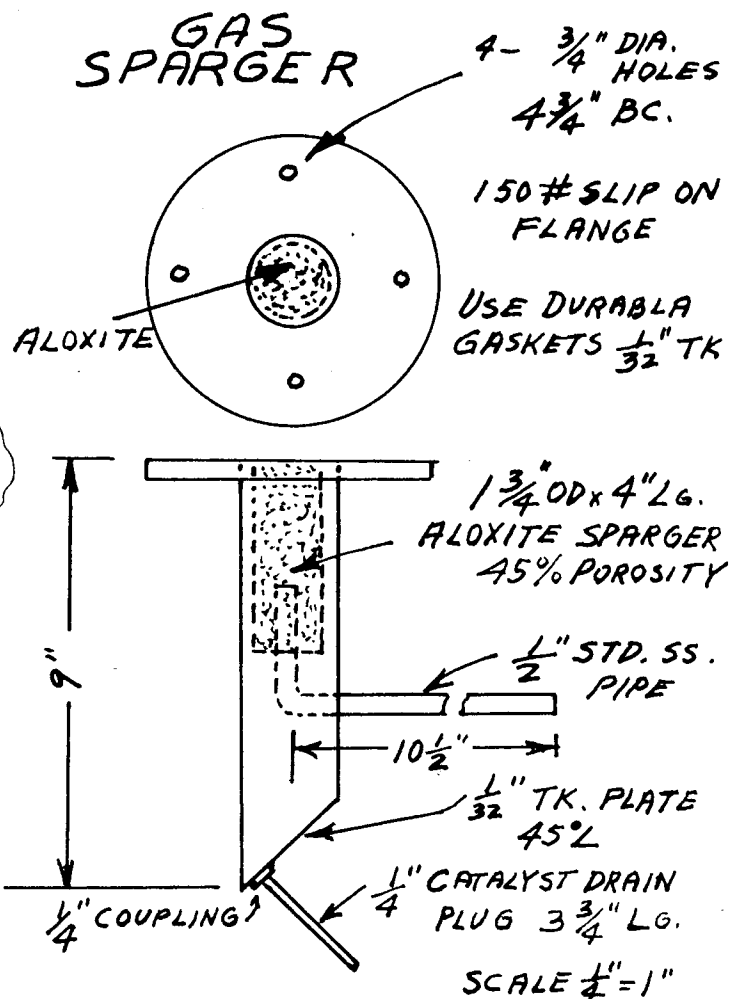
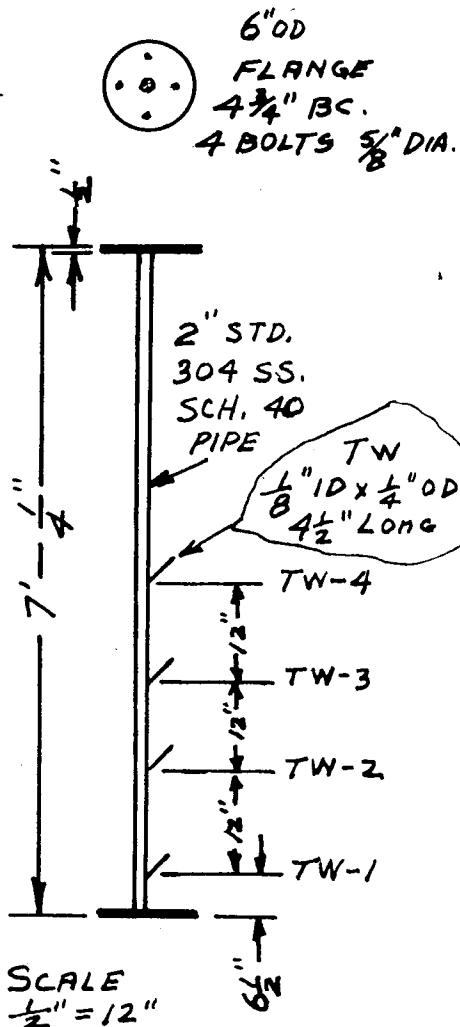


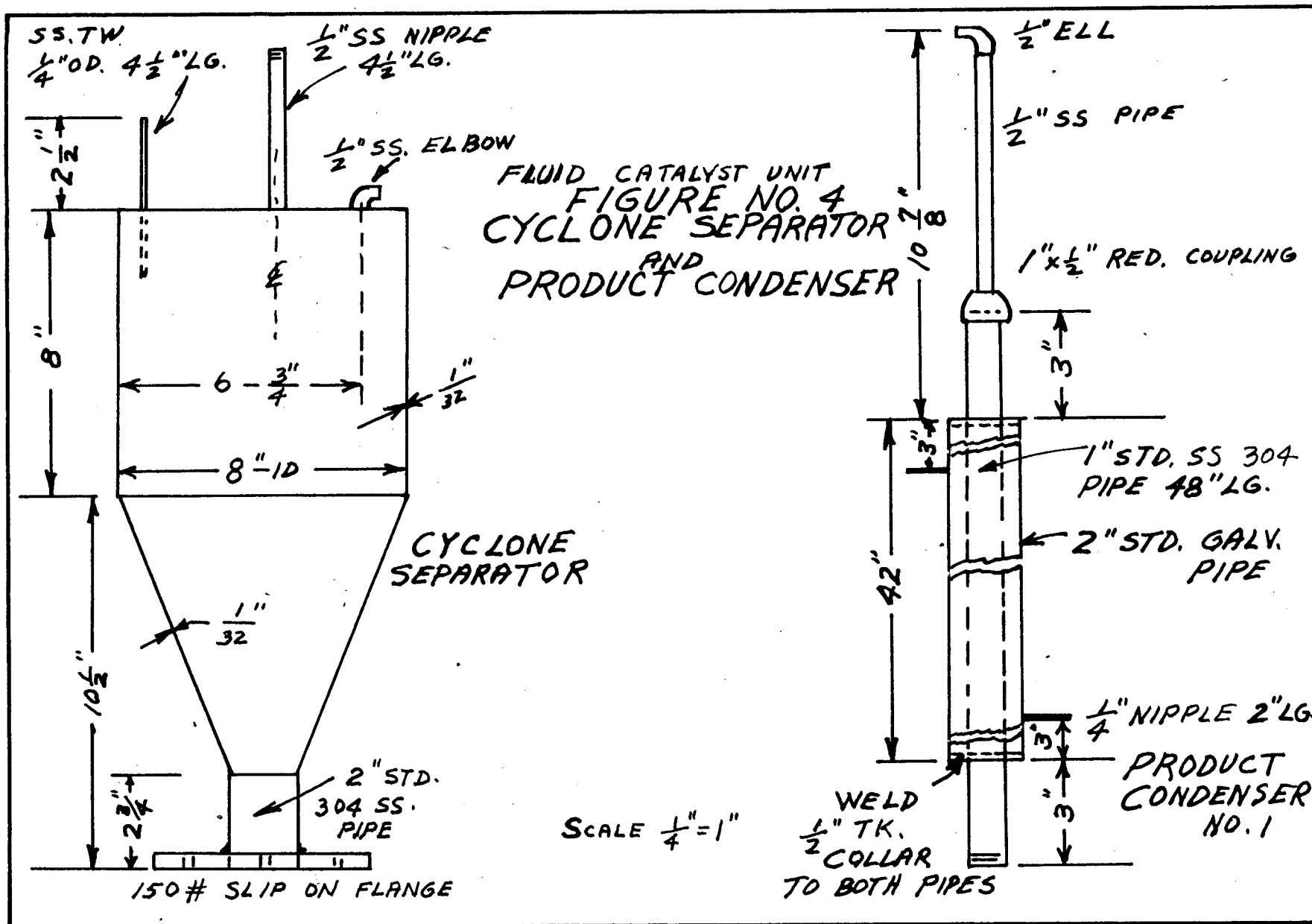
FLUID CATALYST UNIT DETAILS

FIGURE NO. 3

REACTOR, GAS SPARGER,
HEATERS

REACTOR





p-CYMENTHENE

The p-Cymene used was supplied by the Matheson Co., Inc. and was Terpene-free grade supplied in glass bottles. This material was water white and used as supplied, with no further treatment or purification.

The chemical properties of p-Cymene are:

p-Cymene	$C_{10}H_{14}$
Formula	$CH_3 C_6H_4 CH (CH_3)_2$
Formula Weight	134.21
Form and color	colorless liquid
Specific Gravity	0.857 20/4°C
Melting Point	73.5°C
Boiling Point	176.7°C
Solubility in water	Insoluble.
Solubility in alcohol	Soluble.
Solubility in ether	Soluble.

Vapor pressure data:

<u>Temperature °C</u>	<u>Pressure MM. Hg.</u>
-5.5	0.14
0.0	0.23
0.8	0.25
13.3	0.68
17.3	1.
43.9	5.
57.0	10.
71.1	20.
87.0	40.
97.2	60.
110.8	100.
131.4	200.
153.5	400.
177.2	760.

The vapor pressure equation for p-Cymene as given by Kobe and his co-workers (6) is:

$$\log p = - \frac{2.332}{T} + 8.063$$

METHOD OF OPERATING UNIT

The prepared catalyst was heated and placed in a graduate to measure the amount being used. This catalyst was charged into the reactor by removing the 1/2" cap on top of the cyclone, pouring the catalyst into a small glass funnel and permitting the catalyst to flow into the cyclone and drop to the reactor bottom.

After the catalyst had been added the cap was replaced and the air flow increased to about twice the maximum flow rate desired. This was done in order to sweep out fines from the reactor.

The air compressor operated at high pressure; therefore the 60-75 psig. air was passed through a reducing valve to give 15 psig. air through the air flow line to the calibrated air rotameter. The air flow was controlled by adjusting the valve on the air line just before rotameter proper. All air measurements were taken at 15 psig. and converted to volumes of air at 70°F and atmospheric pressure by means of a calibration curve established for the rotameter by previous air tests using a standard wet gas meter.

Air was permitted to flow through the unit for at least one hour before adding the hydrocarbon vapors.

The electric current was turned on at the two wall switches, and the large powerstat set so as to heat the unit in approximately one hour. The heat was reduced or increased depending upon the temperature desired in the reactor. The small powerstat was also turned on in

order to heat the hydrocarbon feed line from the pump discharge to the inlet of the reactor and also supply heat to the bottom of the sparging section.

The temperature of each column section was checked by means of a Leeds & Northrup potentiometer, using iron-constantan thermocouples. Since No. 2 thermocouple registered a few degrees higher than No. 1 and No. 3, this point was used as a temperature control point for runs No. 1 to No. 6. This thermocouple was also located in the center section of the fluid bed.

The reactor temperature was set at 20-25°C below the desired reaction temperature since oxidation would result in additional heat and higher temperature.

As soon as the reactor temperature had been stabilized to the desired operating value, the feed pump was turned ^{on} and liquid p-Cymene was pumped from the 1,000 ml. graduate through the heated feed line, vaporized, mixed with the air stream and entered into the gas sparging section of the reactor. The vapors passed through the sparger and contacted the catalyst particles, reacted and passed through the cyclone and into the condenser where the p-Cymene reaction products and unreacted material condensed and flowed into the product receiver. Uncondensable gases passed out through the set of three condensers and three product receivers, through the carbon trap and through a gas line to the outside atmosphere. Provision was made to take a sample of the gas leaving the carbon trap. The gas was analyzed for CO₂ content by

means of a portable Orsat apparatus. It was desired to keep the CO₂ content below 4 per cent in order to prevent excessive coking on the catalyst.

The feed rate was determined by measuring the quantity of p-Cymene pumped through the unit. The air continued to flow for at least 30 minutes after the feed had been stopped. This was done in order to sweep out all traces of hydrocarbon which may have been in the unit. The heat was turned off and the products collected in the three receivers were combined. The condensers, vapor lines and receivers were washed with water and this was tested for acids.

The carbon trap was removed from the unit and steamed to recover p-Cymene adsorbed. This p-Cymene, amounting to about 10 cc. in highest air flow run, was added to the product collected. Analysis was made of the oil layer and the water layer obtained in each run.

The length of each run was limited to one hour.

It was found that the carbon trap was not large enough to recover all the p-Cymene in the vapor. However since this work was only exploratory it was decided not to change the size of the trap at this time.

CATALYST PREPARATION

The following formulation was used for the catalyst preparation.

Formula: Suggested by Ref. (12)

1. 400 cc. distilled water
2. 380 gm. oxalic acid, technical 99% pure.
3. 190 gm. ammonium metavanadate, c.p.
4. 2,000 gm. 60-150 mesh carrier, type H-41 activated alumina.

Procedure:

Add the water to a glass vessel and add (1) the oxalic acid. Solution gets cold. Add (2) ammonium metavanadate; stir well. The solution turns from water white to yellow, to orange, to red brown, to bluish green and finally dark blue. Considerable gas is given off and some catalyst liquid carried over by entrainment.

Heat the solution to 70°C to obtain quicker solution and to complete the chemical reaction. After ten minutes the solution is completed and a clear blue colored liquor results. Add the carrier, let catalyst soak up all of the liquor. Add a little more water so that only a trace of blue liquor is found at the bottom of the vessel. Keep stirring and mixing the catalyst carrier until thoroughly mixed and completely saturated with the catalyst solution. Use additional water, if needed, to show presence of excess liquor. Let catalyst stand for twenty minutes, mix well again and spread in a 1/4 inch thick layer on to porcelain or glass drying trays.

Air-dry the catalyst for two days, then place in oven to vaporize all remaining moisture. Finally transfer the catalyst to a porcelain drying dish and heat on a hot plate at low heat. Stir constantly to produce even heating. Considerable moisture will be given off together with other gases. Heat for a period of four hours. Mixture will assume a dark green-gray color. Next heat the same catalyst at a medium heat for four hours, more gas will be given off and the color will turn to a dark green yellow. Again, stir constantly so that air will be available to the catalyst surfaces.

Heat at a high heat, stirring constantly until the catalyst turns a pale yellow green color. Cool and screen the catalyst to proper mesh size. Discard the fines and oversize particles.

CATALYST CARRIER

The catalyst carrier selected for this test work was type H-41 Activated Alumina. This material was supplied by the Aluminum Ore Company of Pittsburg, Pa., to the Aluminum Company of America and shipped to the writer for test purposes.

The formula for this very reactive Alumina gel is $Al_2O_3 \cdot xH_2O$. It is an excellent adsorbent and has the following typical adsorption figures when not coated.

<u>Relative Humidity</u>	<u>Adsorption at 100% Efficiency</u>
20%	10%
40%	14%
60%	24%
94%	34%

It appears to have hard, glassy granules, is fully activated and has the following approximate chemical analysis:

Loss On Ignition	8.5%
Si O ₂	5.5%
Fe ₂ O ₃	0.12%
Na ₂ O	0.10%
Al ₂ O ₃	90%

The carrier was screened to obtain 60-150 mesh particle size for this study.

Surface Area, sq. meters per gram, 200-300.

Porosity

50%

Heat Resistance: heated for 24 hours at 500°C., 241 sq. meters per gram, and when heated for 2400 hours at same temperature, the surface area decreased to 216 sq. meters per gram.

This catalyst carrier had to be abandoned due to its high activity rating of 44.1 resulting in complete combustion of the hydrocarbon. In its place another carrier was more successful. This was the Norton catalyst labeled catalyst "D" in the test runs. The activity of the Norton catalyst was 11.

DESCRIPTION OF TESTED CATALYSTS

Catalyst "A" - - 60 to 150 mesh Alumina H-41 carrier impregnated with Vanadium oxide catalyst as described under "Catalyst Preparation".

Catalyst "B" - - No. 902 Davidson. Silica Gel carrier coated with Vanadium oxide catalyst and modified with alkali. Fines than 270 mesh.

Catalyst "C" - - No. 902 Davidson catalyst diluted with inert Norton carrier LA-232. Fines than 270 mesh. Dilution used. 200 cc Davidson active catalyst and 300 cc Norton inert carrier.

Catalyst "D" - - Norton carrier LA-232, 16 to 60 mesh size and impregnated with Molybdenum-Chromium catalyst solution prepared by dissolving 0.50 gm. Chromium Trioxide and 60 gm. Ammonium Molybdate in 500 cc ratio. Catalyst stirred in solution and placed on hot plates to evaporate to dryness. Stirred constantly until dry. Then oxidized until yellow oxide obtained from brown-gray mass.

Activity tests made for each catalyst reported in Table II.

CODE 902

P OWDERED
OXIDATION CATALYST
(Fluid technique)

Physical Form

On 80 mesh	8.0% max.
On 100 mesh	15.0% max.
On 200 mesh	55.0% max.
Thru 200 mesh	45.0% min.

Chemical Composition

Vanadia	10%
Silica	75%
Potassium Sulfate	33%

Activity

10-20 mesh catalyst activated for 2 hours at 800°F. placed in a test unit was run under the following conditions for the conversion of naphthalene to phthalic anhydride:

Jacket Temperature	720°F.
Primary Air	120 CC. /min.
Secondary Air	550 cc. /min.
Space Velocity	1400/V/hr.
Air/naphthalene ratio	36:1/weight ratio
Volume of catalyst	33 cc. (Poured Volume)
Catalyst space in reactor	2 x 10 cm.
Naphthalene used	Baker's C. P.

Results:

Yield Phthalic Anhydride	91.1% based on naph. feed
Carbon Balance	95.2%
Hot Spot Temperature	851-866°F.

Potential Applications

Oxidation of:

Naphthalene
Benzene
Micro-Crystalline Waxes
Aliphatic Side Chains
Furfural and Related Compounds
Ortho-xylene
Quinoline
Toluene

CATALYST ACTIVITY RATING

Whenever catalysts are to be used for oxidation work they should be checked for standard activity rating by at least one method. A suggested method is the use of the Aromatic Adsorption Index method described in the literature and used by the petroleum companies since 1943. The writer has used this method since 1945.

AROMATIC ADSORPTION INDEX METHOD (AAI.)

This method is the most widely used and is fairly rapid and simple. It depends upon the selective adsorption of toluene from a toluene-iso-octane solution by the catalyst under test. The method involves the following steps:

1. Establishment of the specific gravity at 68/68°F for various percentages of toluene-iso-octane mixtures from 0 to 30 percent by weight toluene.

A list of values for this straight line curve are:

<u>Sp. Gr.</u> <u>68/68°F</u>	<u>Wt.</u> <u>Percent</u> <u>Toluene</u>
0.6925	0
0.6991	5
0.7079	10
0.7140	15
0.7210	20
0.7286	25
0.7367	30

2. Establish a straight line curve for the small range used, 0 to 40 volume percent toluene, in toluene-iso-octane solutions at 77°F., as a function of refractive index values at 68°F.

A list of values for this system is:

<u>Vol. % Toluene</u>	<u>R. I. at 68°F.</u>
2.5	1.39342
5.5	1.39628
15.7	1.40653
20.3	1.41175
25.0	1.41663
30.0	1.42121
39.5	1.43160

The above values, when plotted, will give a curve "A".

Another curve is plotted of RI vs Wt. Percent Toluene. (Curve "B").

The procedure employed in this test is as follows: Place a watch glass on the balance and obtain the weight of the glass empty. Weigh 35 gm. of catalyst and place the catalyst in the 100 cc. pyrex adsorption bottle. (Wide mouth bottle used.) Pipette 50 cc. of toluene-iso-octane test solution at 68°F. and place in the adsorption bottle. Stopper immediately using a ground glass stopper and place a rubber band around the stopper to keep it in place. Shake gently to wet all catalyst. Let stand at room temperature of 77°F for 2 hours, shaking at 15 minutes interval. Cool in ice bath and filter through filter paper into a cold 2-ounce bottle. Cover funnel with watch glass during filtration in order to prevent evaporation losses.

Determine the specific gravity of the solution at 68°F.

Example:

Wt. of pycnometer + sample	36.0095 gm.
Wt. of pycnometer	<u>27.6359</u>
Wt. of sample	8.3736 gm.
Volume of pycnometer at 68°F	11.4112 cc.
Sp. gr. 68/68°F = $\frac{\text{wt. sample}}{\text{volume}}$	$\frac{8.3736}{11.4112} = 0.7338$

From curve "B" determine the toluene concentration of the original solution and the filtered solution. The filtered solution may be 23.98 weight percent for 0.7338 sp. gr. while the original solution may have been 25.48 weight percent toluene. The decrease is $25.48 - 23.98 = 1.50$ percent toluene change due to adsorption by the catalyst.

To obtain the Aromatic Adsorption Index multiply by 10.55, a constant, to obtain 15.82 as the AAI value. (1% toluene change = 0.001055 RI. change at 68°F.) Next use curve 8 and read the corresponding Standard Activity Rating for a value of 15.82 AAI. This value will be found on the curve to be 26.2 Standard Activity Rating.

Therefore, one Aromatic Adsorption Unit, expressed as AAI, is equal to 0.1 percent toluene concentration change and the Standard Catalyst Activity is related to the number of AAI units by empirical correlation.

Values for Curve 8 employing synthetic catalysts of various types are as follows:

<u>Aromatic Adsorption Index</u>	<u>Standard Activity Rating</u>
0	0
2.2	6
4.2	12
11.0	20
19.0	30
29.0	40
43.7	50
65.7	60
85.0	66

Plot on rectangular coordinates.

Ref.: Data published by Texas Company. 1945.

A decrease of 1 AAI unit is equivalent to a 5% decrease in cracking activity on a weight basis. Therefore a 5% decrease in space velocity or some other equivalent changes must be made in order to keep the conversion figure constant.

Good operating conditions for cracking catalysts indicate a value of 25-30 AAI units, while fresh catalyst not stabilized shows 50 to 70 AAI units. However, oxidation catalyst operate at lower values of AAI, generally in the range of 3-6 AAI units. The following table lists a comparison of various catalysts tested by the writer in order to compare oxidation catalysts.

<u>CATALYST</u>	<u>STANDARD CATALYST ACTIVITY</u>
1. 90% U_2O_5 , 5% MnO_3 , 5% CrO_3 on 6-8 mesh inert carrier Al_2O_3 Refractory type	5.4
2. Same catalyst reduced to 70-100 mesh	5.4
3. Same catalyst on 4-12 mesh carrier	7.4
4. Same catalyst on 60-150 mesh carrier	11.0
5. Same catalyst on 150-250 mesh carrier	13.0
6. Same catalyst on 150 and finer	13.0
6a. Same catalyst on 80-150 mesh silica gel	26.7
7. American Cyanamid Cracking Catalyst Grade MS-A	59.2
8. Silica Gel 80-250 mesh	64.0
9. Chromium Oxide (Sesqui oxide)	13.0
10. Pumice FFF (passes 250 mesh)	3.0
11. Vanadium oxide powder	5.4
12. General Ceramics Stoneware Carrier	7.4
13. Dicalite 622-7 Carrier	4.6
14. Dicalite 654 SF grade	0.0
15. Dicalite 621-T, SA-5 grade	0.0
16. Zircon Carrier 60-200 mesh	5.6
17. Vanadium oxide on Alumina Oxide	44.1
18. Catalyst 902 on silica gel	--

This table indicates the wide range of Activity encountered in catalyst preparations and points out that pumice would be the best carrier beside Dicalite, which is rejected due to its excessive fine-

ness. The table also definitely discourages the use of silica gel and activated alumina for oxidation use but would recommend these for cracking usage. An examination of various catalysts used by the writer disclosed that almost all oxidation catalysts for aldehyde production possessed a catalyst activity rating somewhere in the range of 5 to 13 Units. It is therefore suggested that investigation of this factor be carried further in order to properly select good aldehyde producing catalysts for vapor phase conversion.

RECOMMENDED CATALYSTS FOR VAPOR PHASE OXIDATIONS

Use oxides of Uranium, Molybdenum, Chromium, Copper, Silver, Iron-Vanadium-Chromate, Nickel, Antimony, Bismuth, Tungsten, Tantalum, Tin, Cerium, Cobalt and Platinum.

Recommen

Best combination of catalysts recommended in U. S. Patent 1,636,854 is 7.0% Molybdenum Oxide and 93.0% Uranium Oxide to produce 9.6% benzaldehyde. This would also serve for other aldehyde production.

TEST RUN FOR ACTIVITY OF CATALYST

The catalyst was tested with toluene in order to reduce the over-activity which is common to all freshly prepared catalysts. The unit was heated to 400°C before toluene was vaporized and fed into the reactor. An air flow rate of 0.32 CFM was used at a space velocity of 316. The presence of benzaldehyde in the product was easily recognized by odor and also by the residue oil left after vaporization of the toluene. A small amount of water showed the presence of combustion products of toluene and showed that vanadium catalyst may be used for the production of benzaldehyde from toluene in a vapor phase system.

Two such tests were made using two different sources of toluene. The first sample had the odor of sulfide which was present in the product and was therefore discarded and a reagent grade toluene, thiophene free, was used for the second trial. No sulfide odor resulted with the second sample and the presence of benzaldehyde was again noted in the product.

METHOD OF ANALYSIS

The condensate in the three product receivers were combined and proportional parts of the oil layer and the water layer were taken for analysis. The oil layer was analyzed as follows:

1. A sample of the oil layer was dissolved in 50 percent methanol and titrated with 0.1N NaOH to obtain a total acidity value.
2. Another sample of the oil layer was neutralized, Hydroxylamine Hydrochloride added and the hydrochloric acid liberated in order to obtain the total aldehyde value.
3. A large portion of the oil layer was shaken with a 10 percent sodium carbonate solution. A separation was made yielding a water layer and an oil layer.
4. The water layer was treated with hydrochloric acid to liberate organic acids. The mixture was filtered and ether added to extract the soluble p-toluic acid while insoluble terephthalic precipitates out and was filtered off and titrated separately.
5. The oil layer obtained in (3) was treated with sodium bisulphite to form a bisulphite addition product. This mixture was filtered yielding the clear unreacted p-cymene and a mixture of solid material containing aldehydes and ketones. The mixture was acidified with hydrochloric acid to liberate the aldehydes and ketones. The products were separated by fractional distillation and identified by comparison of the physical constants of the recovered materials and literature values.

6. The water layer in (3) was treated as follows: a sample was titrated with 0.1N NaOH in order to obtain the total acidity of the water phase.

7. Formaldehyde was determined by neutralizing a portion of the water layer to a thymol phenolphthalein end point, adding standard sodium sulfite solution and titrating to the same end point with standardized acid solution.

$$\% \text{ Formaldehyde} = \frac{\text{acid titer} \times \text{normality of acid} \times 3.008}{\text{wt. of water sample}}$$

8. Another portion of the water layer was extracted with ether to remove organic acids. The ether was evaporated and the organic acids identified.

TABULATED RESULTS

The data obtained, tabulated in Tables I to VII following this page, show various runs made at different conditions of temperature, space velocity and mol ratios of air to p-cymene.

The operating conditions are listed in Tables I, II and III and the products in Tables IV, V and VI.

Table VII shows the temperature distribution in various parts of the reactor.

2" Dia. Stainless Steel Reactor

Vapor Phase

Fluid Bed Unit

1 Hr Run

TABLE I.

Catalyst Operating Conditions

Run No.	Catalyst	Wt. Catalyst Gm.	Volume Catalyst cc.	Bed Height In.
1	A		1750	34
2	A		1750	34
3	A		1750	34
4	A		1750	34
5	A		1750	34
6	A		1750	34
7	A	(325 cc inert carrier below sparger top)		
8	B		200	3.8
9	B		200	3.8
10	C		500	9.7
11	C		500	9.7
12	C		500	9.7
13	C		500	9.7
14	D	782	625	12
15	D		625	12

Operating Conditions - Air Flow

TABLE II

Run No.	Catalyst Activity Rating	Air RM Reading	Air CFM 60°F	Space Velocity Sv liters
1	44.4	4.0	0.318	25.8
2	44.4	4.0	0.318	40.9
3	44.4	4.0	0.318	55.5
4	44.4	4.0	0.318	69.3
5	44.4	2.0	0.162	57.3
6	44.4	7.9	0.638	49.0
7	44.4	No Run Completed. Excessive carbon on catalyst.		
8	Note	6.0	0.461	287
9	Note	4.0	0.319	245.6
10	11	4.0	0.319	248
11	11	4.0	0.319	257
12	11	4.0	0.319	257
13	11	4.0	0.318	127
14	11	10	0.883	59.6
15	11	10	0.883	59.6

Note: Not determined but behaved very energetic indicating a rating greater than 11 for the diluted catalyst bed C.

AIR OXIDATION OF P-CYMENE
Operating Conditions - Feed Rates

T A B L E I I I

Run No.	Reaction Temp. F Average	<u>P-Cymene Charged</u>		<u>Mol Air</u>
		<u>cc/hr</u>	<u>Gm/hr</u>	<u>Mol p-Cymene</u>
1	915	257	220	14.00
2	720	440	377	8.15
3	682	620	531	5.78
4	585	788	675	4.55
5	530	670	574	2.72
6	500	480	412	14.90
7	—	—	—	—
8	520	920	788	5.65
9	630	800	685	4.50
10	560	810	694	4.43
11	790	840	720	4.27
12	890	840	720	4.27
13	910	385	330	9.31
14	910	225	193	44.1
15	980	225	193	44.1

Products

TABLE IV

Run No.	T-S Feed Preheat Temp. °F	% CO ₂ Exit Gas	Oil Products		Water Product Gm/Hr
			cc/Hr	Gm/Hr	
1	165	—	92	80	80
2	160	2.7	680	585	130
3	175	2.5	388	325	80
4	175	1.1	318	275	50
5	173	3.1	550	473	60
6	171	0.1	398	342	—
7	—	—	—	—	—
8	176	0.0	880	755	—
9	176	0.0	755	649	—
10	95	0.0	785	675	—
11	105	1.5	780	670	—
12	105	2.9	760	656	—
13	107	4.1	310	267	—
14	80 x	0.1	160	138	0
15	85 x	9.0	148	128	38

x Not accurate due to intermixing of air stream at high flow.
Thermowell too near air flow mixing tee junction.

AIR OXIDATION OF P-CYMBENE

Analysis of Products

TABLE V

Run No.	Wt. P-Toluic Acid Oil Layer	PRODUCTS		GM/HR	Acid in Wash Water as P-Toluic
		Terephthalic Aldehyde Oil Layer			
1	0	0			—
2	0	0			—
3	0	0			—
4	0	0			—
5	0	0			0.83
6	—	—			0.019
7	—	—			—
8	3.99	11.7			0
9	3.72	12.9			0
10	4.04	8.1			Trace
11	1.53	4.5			0
12	1.56	4.08			—
13	0.96	2.0			—
14	0.72	0.99			Trace formaldehyde
15	3.25	5.37			4.18

AIR OXIDATION OF P-CYMENE

Oil Product Analysis

TABLE VI

Run No.	WT %/ P-Toluic Acid	WT %/ Terephthalic Aldehyde	Product Receiver Temp. °C
1	0	0	26
2	0	0	24
3	0	0	24
4	0	0	25
5	0	0	27
6	0	0	25
7	—	—	—
8	0.527	1.55	24
9	0.574	2.0	24
10	0.598	1.2	24
11	0.229	0.68	25
12	0.239	0.62	25
13	0.359	0.75	25
14	0.52	0.72	28
15	2.55	4.20	29

Temperatures at Various Positions
of Reactor. of

T A B L E VII

Run No.	T-1	T-2	T-3	T-4	T-6 Overhead Cyclone
1	885	917	915	655	150
2	680	720	720	430	250
3	645	682	670	445	275
4	560	585	565	320	225
5	515	530	500	315	280
6	467	500	408	280	—
7	—	—	—	—	—
8	520	Note	Note	Note	210
9	630	Note	Note	Note	218
10	275	390	560	560	195
11	440	665	790	475	180
12	415	725	890	535	230
13	380	665	910	640	250
14	630	730	910	600	160
15	930	980	950	725	190

Note: Values too low indicated no catalyst near thermowell.
No record taken of low temperatures.

EFFECT OF SPACE VELOCITY

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Space velocity is defined as the volume of air used per hour per volume of catalyst space, or

$$\text{Space Velocity} = \frac{\text{liters of air + p-cymene}}{\text{hours} \times \text{liters of catalyst space}}$$

The effect of Space Velocity calculated for the various runs and listed in Table II shows the following conditions for maximum yield of aldehyde.

Reaction Temperature	980°F
Space Velocity	59.6 liters
Mol ratio, air to p-Cymene	44.1
CO ₂ in exit gas	9.0%

EFFECT OF AIR TO HYDROCARBON RATIO

The effect of the mol ratio of air to p-cymene apparent from this work is that relatively large amounts of air are needed even for aldehyde production. The runs were made at very low air to p-cymene mol ratios in order to obtain more aldehyde than acid formation. However, since this program was not expanded far enough no definite statement can be made on the proper ratio to use for maximum production of aldehyde.

EFFECT OF TEMPERATURE

No heat balance was made on this unit. For a detailed heat transfer study of reactors and converters the reader is referred to the work of Gustav Wirth (18).

The effect of the temperature range employed in this work shows the values of 470°C as being the lower limit of oxidation and approximately 530°C as being the upper limit before appreciable decomposition of the p-cymene occurs, resulting in complete oxidation to volatile acids, carbon dioxide and water.

The recommended operating temperature appears to be approximately 515°C at a mol ratio of air to p-cymene of 44.1. These conditions would apply only to Catalyst "D".

SUMMARY OF LIQUID PHASE OXIDATION

Examination of data of Senseman and Stubbs (16) for the liquid phase oxidation of p-cymene discloses 170°C as most practical reaction temperature giving a p-toluic acid yield of 33.1%, based upon the p-cymene in the charge, and a maximum time of reaction of 5 hours as the most practical condition.

Smart Of L

The work presented shows that the catalyst activity must first be of a low value in order to have the oxidation controllable and resulting in useful oxidation products other than carbon dioxide and water. Runs 1 to 6 showed complete combustion due to a high activity catalyst carrier, activated Alumina H-41.

Catalyst D gave the best production rate if compared to the amount of feed charged. The production rate can be increased materially by increasing the oil and air feed in proper proportions. The only limiting factor to consider is the particle velocity as the catalyst must be kept in the reactor at the flow condition. Increase in bed height would be necessary also if the reactor diameter remains the same.

The following conclusions ~~are reached~~ ^{can be drawn} from this exploratory work:

1. A low activity catalyst carrier must be used. Should be below 11 in activity rating.
2. An aldehyde producing catalyst should be used in preference to acid producing catalysts as operating controls would be easier to maintain. Suggest Molybdenum-Chromium, Uranium, Tungsten combinations.
3. Temperature must be sufficiently high to show partial combustion and formation of water and carbon dioxide. Measurement of carbon dioxide formation would be good process control method.
4. Proper control of the air to p-Cymene mol ratio will give the proper product required, aldehyde in preference to acid.

SAMPLE CALCULATIONS

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Air CFM₆₀₀ = Air Rotameter reading corrected to 60°F.

For Run 1. Air Rotameter reading = 4.0 which corresponds to 0.325 CFM at 72°F and 1 atm. correct to 60°F and 1 atm. by factor

$$= \frac{(460 + 60^\circ\text{F})}{(460 + 72^\circ\text{F})} \times 0.325 = 0.319 \text{ CFM}$$

Space Velocity = Liters of air + liters of gaseous p-cymene per liter of reactor volume per hour.

Space Velocity = Sv liter

$$\text{Sv} = \frac{\text{air} + \text{p-cymene}}{\text{Volume reactor} \times \text{hr}}$$

For Run 1. p-cymene charged = 257 cc/hr.

$$\text{gm/hr.} = \frac{257 \text{ cc.}}{\text{hr.}} \times \frac{0.857 \text{ gm}}{\text{cc}} = \frac{220 \text{ gm}}{\text{hr}}$$

$$\frac{220 \text{ gm}}{134.21 \text{ gm/mol}} = 1.64 \text{ moles p-cymene}$$

$$1.64 \text{ moles} \times 22.4 \text{ liters at } 32^\circ\text{F} + 1 \text{ atm.} = 36.7 \text{ liters}$$

$$\therefore \text{Sv} = \frac{853 + 36.7}{1.750 \times 1 \text{ hr}} = 40.9$$

$$\text{liters air at } 32^\circ\text{F} = \text{CFM}_{600^\circ\text{F}} \frac{(460 + 32)}{(460 + 60)} = 0.318(.945)(28.32)$$

Sample Calculations (continued)

$\frac{\text{Mol air}}{\text{Mol p-Cymene}}$	Calculation.
Gm. air	$= \frac{(\text{CFM})(\text{Min})(29 \text{ /Mol})453.6 \text{ gm/}}{378 \text{ cu. ft./mol.}}$
Gm. air	$= (\text{CFM})(\text{Min})(34.78 \text{ factor})$
$\frac{\text{Mol air}}{\text{Mol p-Cymene}}$	$= \frac{(\text{CFM})(\text{Min})(34.78) \text{M.W. p-cymene}}{(\text{gm p-cymene})(\text{M.W. air})}$
$\frac{\text{Mol air}}{\text{Mol p-Cymene}}$	$= \frac{(\text{CFM})(\text{Min})(34.78)(134.32)}{(\text{gm p-cymene})(29)}$
$\frac{\text{Mol air}}{\text{Mol p-Cymene}}$	$= \frac{(\text{CFM})(\text{Min})(160.8 \text{ factor})}{(\text{gm p-cymene})}$

For Run 1.

$$\frac{\text{Mol air}}{\text{Mol p-cymene}} = \frac{(0.319)(60)(160.8)}{220} = 14.0$$

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