

# CATALYTIC OXIDATIONS of NAPHTHALENE SERIES

▶ ▶ ▶ Vapor-phase catalytic oxidations were made on commercial naphthalene, practical Tetralin, 95 per cent 2-methylnaphthalene and 70 per cent 1-methylnaphthalene to yield chiefly phthalic anhydride. Quinone by-products were found in small amounts. The most successful catalyst consists of pure pyrolytic vanadium pentoxide fused on glassy silica gel. A tin-bearing vanadium catalyst was tried with but moderate success.

Two complete oxidizers were built and details of construction are given. A small apparatus made entirely of Pyrex was used for systematic investigation of space velocity and yield relations. A stainless steel Downs-type oxidizer was employed for check runs. The maximum yields of phthalic anhydride were 76 per cent from naphthalene, 70 per cent from Tetralin, and 40-50 per cent from methylnaphthalenes.

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THE process variables involved in catalytic vapor-phase oxidation of aromatic compounds are space velocity, or contact time which is its reciprocal function, temperature, the ratio of the reactants, and the nature of the catalyst. Unfortunately in the past, investigators of these reactions have failed to correlate and, in many cases, even to record all their findings on these salient data. The result is that, although the reaction of air on naphthalene vapor to produce phthalic anhydride has been used commercially for at least twenty years, very little detailed and specific information appears in the public print.

This investigation was undertaken to supply some of the missing information, especially that pertaining to problems involved in carrying out such reactions successfully, control of apparatus, behavior of catalysts, nature of the crude products, and possible relations between the process variables. In addition, information has been obtained about the oxidation of substituted naphthalenes which have been studied very little until now.

## Glass Oxidation System

Figure 1 shows the small Pyrex apparatus used for systematic investigation of space velocity and yield relations. The vaporizer was made from a 100-cc. Kjeldahl flask and was heated by immersion in a bath of molten paraffin wax, the temperature of which was measured by a mercury thermometer. The preheater, which had a coil height of 6-7 inches and a length of about 60 inches, was made of 8-mm. Pyrex tubing. The catalyst tube, which contained 30-40 cc. of catalyst, was constructed from 25-mm. tubing, with the central downcomer 8 mm. in outside diameter. The annular catalyst bed, the top half inch of which was visible above the bath, was supported by a plug of glass wool; the catalyst temperature was measured by a bare-tipped chromel-alumel thermocouple located in the center of the annular catalyst layer, 1.5 inches from the top of the four-inch long bed. The annular layer was about 1/4 inch thick. The salt bath was a mixture of 40 per cent sodium nitrite, 7 per cent sodium nitrate, and 53 per cent potassium nitrate (16) contained in a steel pot, gas-fired and agitated by a propeller. The bath temperature was measured by a chromel-alumel thermocouple. The air-cooled condenser tubes were 1.5-foot lengths of 25-mm. Pyrex tubing; the spare was used in case of plugging of the main system. The

hot ends of these tubes were sealed to the catalyst-tube offtake with built-up stoppers of asbestos paper. The cold trap tube, 35 mm. in diameter was immersed in a carbon tetrachloride-chloroform mixture contained in a Dewar bottle and cooled with solid carbon dioxide. The Cottrell precipitator was made from 25-mm. Pyrex and bore a central electrode of 1/16-inch steel rod and an outer electrode 1 foot long made from copper window screen.

The air was passed first through a 1-gallon "ballast bottle" to smooth out flow irregularities; it was measured by a differential-water-column flowmeter and mercury-filled manometer. The metered air was introduced directly into the vaporizer. These metering and gas handling devices are not shown in Figure 1.

It is unnecessary to dry or decarbonate the air for these oxidations (?). An auxiliary stream of measured air was used for cooling and aerating the catalyst.

All bare unheated parts were insulated with asbestos rope. The vaporizer outlet tube was heated electrically. The reaction tube, preheater, and vaporizer were sealed in series with useful temporary, tight, heat-resistant joints built up from layers of asbestos paper soaked in water glass, alternated with windings of fine copper wire.

## Downs Metal Oxidation System

Figures 2 and 3 show the steel Downs-type reactor used for check runs to approximate commercial conditions on a one-tube scale. The air was measured and controlled in a manner similar to the small oxidizer except that two air streams were required in normal operation. The vaporizer and air preheaters were heated by immersion in molten paraffin, the temperature of which was measured. The reaction preheater tube of stainless steel was heated by a small electric tube furnace constructed by winding 8.5 feet of 1/8 × 0.0201 inch Nichrome ribbon (about 2 ohms) on a cylindrical alundum core, 1 foot long and 1 1/16 inches i. d. The element was covered with refractory cement, and the unit was insulated by packing with Sil-O-Cel.

The reactor was the type using boiling mercury to remove the heat of reaction; the boiling temperature was regulated by nitrogen pressure on the mercury condenser system. The catalyst tube was a 1-inch stainless-steel pipe welded through the center of a steel jacket, 4.5 inches in diameter and 1 foot long. The tube and jacket were mounted in an electric furnace constructed similarly to the reaction preheater. The alundum core was 1 foot long and 4 9/16 inches i. d. The heater element was a 40-foot length of 1/8 × 0.0126 inch Nichrome V



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ribbon (approximately 20 ohms) with an extra center-tapped lead. The unit was constructed in a three-legged pot made from 10-inch steel pipe. Figure 4 shows the heater circuit.

The catalyst was supported on a small screen at the level of the jacket bottom, held up by prongs on a thermocouple well extending into the bottom of the tube. The catalyst temperature was measured by chromel-alumel thermocouples buried in the entering and exit layers of the catalyst. The entering thermocouple was bare, the exit sheathed in a thin tubular well. The former was introduced through the packed blank-flange joint at the top of the tube. This flange may be used as an inlet for several thermocouples if desired. The thermocouple circuit is shown in Figure 5.

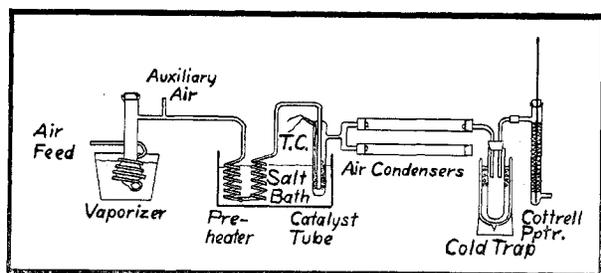


Figure 1. Small Glass Oxidizer

The air-cooled condenser was a 2-foot length of 1-inch Pyrex pipe, followed in the condensing system by an air-cooled trap bottle. The Cottrell precipitator (Figure 2) was made from 50-mm. Pyrex tubing and the screen electrode was 18 inches long. The central electrode consisted of a  $\frac{1}{8}$ -inch welding rod upon which were mounted discharge rings. Power for the Cottrell precipitator was furnished by a pair of 12,000-volt neon-sign transformers with primaries in parallel and secondaries in series. The primary circuit included a rheostat and voltmeter.

A packed water-scrubbing column (Figure 3) containing a bed, 18 inches long and 35 mm. in diameter, of  $\frac{3}{16} \times \frac{1}{4}$  inch glass rings was substituted for the Cottrell precipitator in several runs. The column was fed from the split discharge of a laboratory centrifugal pump which drew water from a 1-liter beaker into which was dipped the bottom drain tube from the column.

Three flowmeters of differential-liquid-column type having maximum capacities of 80, 150, and 600 liters per hour were used singly or in pairs in this study. These meters were calibrated throughout their entire ranges under the usual small superatmospheric operating pressure of the system with a Sargent wet-test gas meter.

### Catalysts

The elements reported as basic catalysts or promoters include most of the cation-forming members of the Periodic Table. More favorable claims for basic materials are narrowed to the Fifth Group elements. Most of the references available are in the patent literature, which is vague at best (2, 19). The oxides of vanadium, molybdenum, tungsten, uranium, and manganese are claimed to give the highest yields of phthalic anhydride from naphthalene (19), with vanadium pentoxide seemingly the one preferred. Tin vanadate has the advantage of lower operating temperature (20).

Not only the composition but the method of preparation and activation are said to have significant bearing on the effectiveness of the catalyst. The catalysts used commercially are basically vanadium pentoxide with all details of modification closely guarded secrets (12). In addition, even

with identical preparation and pretreatment, one of two catalysts of vanadium pentoxide made from different lots of commercial ammonium metavanadate may be highly efficient and the other ineffective (?). Consequently, some experimentation was necessary to secure a catalyst which was sufficiently active, adhered well to the support, and was stable during repeated use.

The vanadium oxides of interest for catalytic purposes are the red-purple to orange pentoxide,  $V_2O_5$ , the blue tetroxide,  $V_2O_4$ , and the green trioxide,  $V_2O_3$  (24). All three have been identified in catalysts after use (25). For catalyst preparation the quinquevalent oxide is available dry by the pyrolysis of ammonium metavanadate or wet as an insoluble, orange, colloidal, or finely crystalline material by acidification of aqueous solutions or suspensions of the metavanadate.

Acid reduction of vanadium pentoxide by sulfurous or oxalic acids results in formation of the more soluble blue vanadyl salts useful for impregnating carriers with higher vanadium concentrations by wet methods. The compounds of this valence stage are blue or reddish brown (24).

**PRECIPITATED VANADIUM PENTOXIDE.** Fifty milliliters of distilled water were saturated near the boiling point with pure commercial ammonium metavanadate ( $NH_4VO_3$ ). Concentrated sulfuric acid was added dropwise to precipitate the hydrated oxide. Evaporation and grinding gave a fine orange powder. Fusion of the powder in oxygen at bright red heat produced dark purplish-red crystals on the crucible sides and a purplish-black glassy mass in the bottom. Re-grinding converted this to a greenish-yellow powder.

**VANADIUM-TIN TRIAL CATALYSTS.** To obtain a low-temperature tin-vanadium catalyst such as that described by Maxted (20), a method based on the Craver patent (9), depending on reduction of vanadates to vanadyl salts with oxalic acid, was used with the addition of stannous chloride dihydrate in ratio of the formula  $Sn(VO_3)_2$ . This catalyst was coated on a very light, porous refractory brick which contained some easily fusible alkali oxides. Such a catalyst was used for runs T-1 MMN, T-1 MN<sub>1</sub>, T-1 and T-2 MN<sub>2</sub>, T-1 T, 1 and 2 MN<sub>2</sub>, 1 to 3 N, and 1 to 3 T, all carried out in the Downs oxidizer. Considerable trouble was experienced with control of the operating temperature of this catalyst,

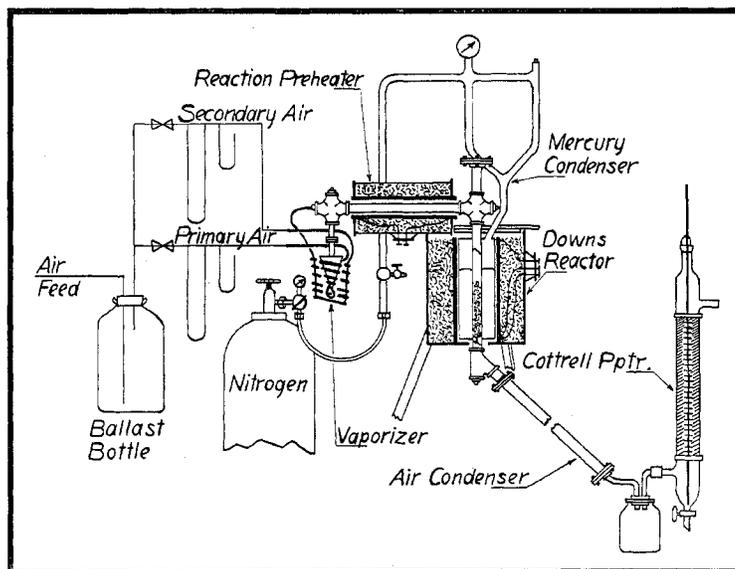


Figure 2. Laboratory Model of Downs Oxidizer

especially after much use. When removed from the tube the catalyst showed evidence of intense fusion.

**VANADIUM PENTOXIDE ON SILICA GEL.** The most successful catalyst was prepared by pyrolytically decomposing ammonium metavanadate and fusing the oxide on commercial glassy silica gel (8-10 mesh) until the carrier was completely coated with the pale purplish-red oxide. This catalyst was used for all controllable runs in the glass reactor as well as for runs 1 and 2 TL, 1 to 3 NL, and 1 to 5 MN<sub>2</sub>L in the large reactor.

### Hydrocarbons<sup>1</sup>

**MIXED METHYLNAPHTHALENES.** Run T-1 MMN was made with technical mixed methylnaphthalenes containing about 65-70 per cent 2-methylnaphthalene as estimated from rough freezing-point studies related to Figure 6 (18).

**2-METHYLNAPHTHALENE.** The runs on 2-methylnaphthalene (MN<sub>2</sub>) were made with commercial white, crystalline material melting above 31° C., of purity above 95 per cent (Figure 6).

**1-METHYLNAPHTHALENE.** A technical-grade synthetic product containing about 70 per cent 1-methyl and 30 per cent 2-methylnaphthalenes, based on approximate freezing points, was used in runs of the MN<sub>1</sub> series.

**TETRALIN.** Practical-grade Tetralin was employed in series T. The only impurities to be expected were traces of naphthalene and Decalin.

**NAPHTHALENE.** The commercial product, melting at 78-9° C., was used in runs of the N series.

### Analytical Procedure

By a series of tests based upon previously reported work (21), it was decided that both 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone could be determined with sufficient accuracy (within 5 per cent of the quinone content of the crude oxidation products, which, in turn, was less than 5 per

<sup>1</sup> In tables and text the hydrocarbons are frequently abbreviated according to the initials e. g., T for Tetralin, N for naphthalene, MMN for mixed methylnaphthalenes, and MLs for 2-methylnaphthalene, etc.

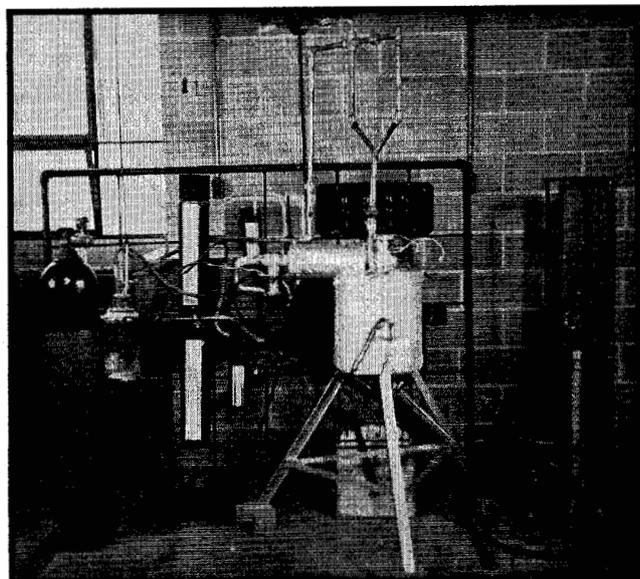


Figure 3. Photograph of Laboratory Downs Oxidizer

Table I. Titration of Quinone in Presence and Absence of Phthalic Anhydride

(Reagents: 0.2 N sodium thiosulfate, unstandardized; 10% KI solution, c. p. conc. HCl; 1,4-naphthoquinone, m. p. 124.5-125° C.)

Sample No.	Quinone, Gram	Phthalic Anhydride, Gram	Thio-sulfate, Ml.	Quinone, M. E.	Thio-sulfate, M. E.	Discrepancy, %
1	0.1016	0.0000	6.74	1.286	1.349	4.9
2	0.1010	0.6778	6.69	1.278	1.338	4.7

Table II. Iodometric Titration of 1,4-Naphthoquinone and 2-Methyl-1,4-naphthoquinone (M. P. 102-3° C.)

(Reagents: 0.103 N sodium thiosulfate, standardized against pure iodine; c. p. conc. HCl; 95% ethanol; pure iodate-free KI)

Sample No.	Quinone, Gram	Thio-sulfate, Ml.	Blank, Ml.	Aging Time, Min.	Quinone by Titration, Gram	Error, %
1	0.1776 (Me-)	23.20	-3.30	2	0.1762	0.8
2	0.1578 (Me-)	19.35	-1.85	10	0.1550	1.3
3	0.1519 (1,4-)	20.16	-1.70	10	0.1501	1.2
4	0.2007 (1,4-)	16.58	-0.24	2	0.2006	0.1
5	0.2009 (1,4-)	17.00	-0.24	2	0.2043	3.4

Table III. Effect of Alkali Titration on Quinones

(Reagents: 0.176 N HCl, 0.905 N NaOH, phenolphthalein)

Sample No.	Quinone, Gram	NaOH, Ml.	HCl, Ml.	NaOH Used, M. E.	Quinone Weighed, M. E.	Error, %
1	0.1589 (1,4-)	5.25	21.05	1.04	1.01	3
2	0.1447 (1,4-)	4.41	17.21	0.96	0.915	4
3	0.1589 (Me-)	4.94	20.45	0.87	0.89	2

cent of the total crude products) by iodometric titration. The data are shown in Tables I, II, and III.

In addition, both quinones acted as monobasic acids in the presence of alkali (Table III). This necessitates a correction of any alkaline determination of true acid constituents of the oxidation products. The acidic behavior of the quinones to alkali probably depends upon the oxidation by air of these substances to the hydroxy-substituted derivatives in basic medium (1).

The procedure adopted for use on the oxidation product consisted of dissolving a 1.00-gram sample of the test solid in 20 ml. of 95 per cent ethanol, adding 20 ml. of concentrated hydrochloric acid with cooling, and dissolving about 2 grams of iodate-free potassium iodide in the resulting solution. The liquid was titrated immediately with standardized sodium thiosulfate solution and starch indicator solution was added near the end point. If the solution was badly discolored by tarry products, the end point was determined by spot test on starch-iodide paper. Aliquot portions of quinone-bearing aqueous wash liquors were titrated by the same procedure, omitting the alcohol.

The weight of quinone present was calculated by the formula:

$$\text{Wt. quinone} = \text{ml. thiosulfate} \times \text{normality} \times \left( \frac{\text{mol. wt. quinone}}{2000} \right)$$

No blank corrections were used. By adding the potassium iodide last and working rapidly, possible errors from absorbed oxygen (26) were minimized; furthermore, liberation of iodine by absorbed oxygen in the reagent mixture on standing frequently did not occur when testing blank samples.

The procedure for determining phthalic anhydride consisted of boiling a weighed 1.00-gram sample of the solid product with 30-40 ml. of distilled water until solution occurred. The solution was cooled rapidly to room temperature and titrated with standardized 1.00 N sodium hydroxide against phenolphthalein (for discolored solutions



indicator paper was used). The weight of phthalic anhydride present was calculated by the formula:

$$\text{Wt. P. A.} = \left[ (\text{ml. NaOH} \times \text{normality}) - \left( \frac{\text{milliequivalents of quinone in weighed sample from quinone analysis}}{1} \right) \right] \times \left( \frac{148}{2000} \right)$$

When yellow aqueous wash liquors were being examined, 10-ml. aliquot portions were diluted to 30-40 ml. and boiled briefly to remove carbon dioxide. The solutions were cooled and titrated in the usual manner, making the quinone correction.

The results are reported as phthalic anhydride because at no time was an appreciable amount of any other organic acid indicated by the alkaline titrations (neutral equivalents) or by the appearance of other than the characteristic phthalic anhydride needles in the condensate, even when operating on methyl-naphthalenes.

A good qualitative test for phthalic anhydride used frequently was the formation of fluorescein by fusion of the unknown samples with resorcinol in the presence of sulfuric acid or other condensing agents (17). When the melt was poured into dilute alkali, a characteristic yellowish-green fluorescence was formed if the unknown contained any phthalic anhydride.

### Tin-Vanadium Catalyst in Glass Reactor

Three runs on 2-methylnaphthalene were attempted with used tin-bearing vanadium catalyst in the small reactor. Air and ethanol vapor were used to try to raise the catalyst to reacting temperature on hydrocarbon. The air-hydrocarbon mixture was substituted when the heat effect in the catalyst seemed sufficiently vigorous. These two streams of material were alternated whenever necessary. Occasionally the catalyst had to be blown with air alone to cool it. A brief summary of the range of conditions tried follows:

Air flow, liters/hour	200-600
Vaporizer temperature, ° C.	90-125
Bath temperature, ° C.	390-450
Temperature of catalyst, reaction going, ° C.	Minimum 500 Maximum 920

The reaction was not self-maintaining in the usual catalytic range, 300-500° C., either on alcohol or hydrocarbon. High space velocities with alcohol were necessary to heat the catalyst to a point where it would maintain hydrocarbon oxidation. To keep the tube from burning up, the velocity had to be reduced as soon as hydrocarbon oxidation was underway. This frequently resulted in "losing" the reaction again. The reaction could be run only intermittently.

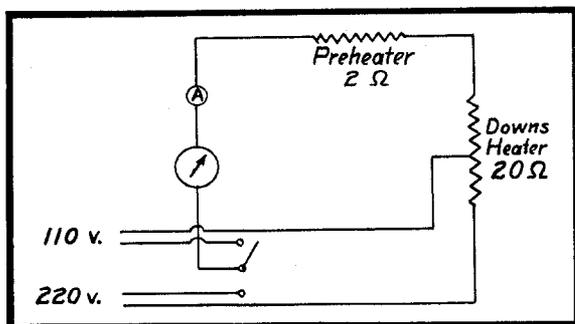


Figure 4. Downs Oxidizer Heater Circuit

The presence of at least one spot in the catalyst glowing at bright red heat and occupying about one third of the catalyst volume appeared to be necessary to maintain the oxidation even intermittently at a partly controlled self-supporting level. In general, this catalyst was uncontrollable after some use and gave only small amounts of tarry and oily oxidation products.

Table IV. Oxidation of Tetralin and Methylnaphthalenes with  $V_2O_5$  on Silica Gel in Small Glass Reactor

Run No.	Space Velocity	Temp., ° C.	Air/Hc. by Wt.	Hc. Wt., Grams	Total Product, Grams	Phthalic Anhydride, Yield %
Tetralin						
1 TS	4450	470	25.0	10	7.5	67
2 TS	2950	465	14.0	10	7.1	63
3 TS	3420	460	17.5	15	9.5	57
4 TS	4830	466	17.0	20	12.4	54
5 TS	5920	465	14.5	20	14.4	61
6 TS	2010	465	15.5	15	11.6	68
7 TS	2010	465	15.0	10	7.7	66
8 TS	2010	440	15.5	10	6.5	56
9 TS	4300	440	16.0	15	11.7	66
10 TS	6100	440	14.5	20	15.8	60
11 TS	7000	454	12.5	25	13.0	44
12 TS	7100	440	12.0	20	12.0	51
13 TS	3780	440	17.0	10	8.1	70
14 TS	5970	464	16.0	20	15.5	65
15 TS	4800	465	15.0	15	11.5	65
16 TS	3260	465	16.5	10	7.0	60
17 TS	2460	460	15.5	10	7.5	65
18 TS			Bad leak in air condenser plugs			
19 TS	5600	466	17.0	15	12.2	68
20 TS	3950	463	18.0	10	8.6	70
21 TS	8130	442	13.1	20	11.7	50
22 TS	8130	460	14.2	20	13.8	58
23 TS	10000	492	12.2	25	14.0	47
24 TS	12120	472	13.1	30	15.9	44
1-Methylnaphthalene						
1 MN <sub>1</sub> S	4540	468	17.6	15	5.5	33
2 MN <sub>1</sub> S	5900	473	13.4	20	Erratic temp.	
3 MN <sub>1</sub> S	5300	465	18.7	15	5.5	33
4 MN <sub>1</sub> S	5280	467	15.5	15	6.0	36
5 MN <sub>1</sub> S	4520	440	16.3	10	4.0	35
2-Methylnaphthalene						
6 MN <sub>2</sub> S	5650	510	18.0	20	4.6	22
7 MN <sub>2</sub> S	2300	475	19.0	20	5.5	25
8 MN <sub>2</sub> S	2950	465	19.0	15	4.3	27
9 MN <sub>2</sub> S	3720	460	22.0	15	4.9	31
10 MN <sub>2</sub> S	4370	465	19.7	15	6.3	40
11 MN <sub>2</sub> S	5920	464	15.5	20	7.4	29
12 MN <sub>2</sub> S	5050	465	16.5	15	5.3	31
13 MN <sub>2</sub> S	2000	443	17.0	10	4.0	35
14 MN <sub>2</sub> S	4270	440	17.0	20	8.3	35
15 MN <sub>2</sub> S	3070	442	20.0	10	4.7	40
16 MN <sub>2</sub> S	5030	465	18.0	15	7.6	43
17 MN <sub>2</sub> S	4120	465	15.6	20	9.5	43
18 MN <sub>2</sub> S	6330	462	16.2	20	6.8	33
19 MN <sub>2</sub> S	6300	464	16.2	20	8.9	35
20 MN <sub>2</sub> S	3000	460	19.8	10	3.9	34
21 MN <sub>2</sub> S	8230	477	17.6	20	8.7	38
22 MN <sub>2</sub> S	10000	485	17.5	20	8.5	39

### Vanadium Pentoxide on Silica Gel in Glass Reactor

Since the vanadium pentoxide catalyst was relatively stable and easy to control, the runs of the Tetralin (TS), 2-methylnaphthalene (MN<sub>2</sub>S), and 1-methylnaphthalene (MN<sub>1</sub>S) series were made in an attempt to correlate yield and space velocity and to observe the nature of the products and the behavior of the catalyst when operating with all the variables under control. Thirty milliliters of the catalyst were used, and it was kept hot and well aerated continuously when not in use. The runs were made on hydrocarbon alone.

The air rate, vaporizer temperature, and salt-bath temperature were set ahead of time. A weighed quantity of hydrocarbon was charged to the vaporizer and the air stream diverted into it. The reaction was followed by observing the catalyst thermocouple readings. Minor adjustments of the controls were made as necessary. The reaction was timed from the start of air flow through the vaporizer until the hydrocarbon bubbled no more and the catalyst temperature fell steadily. At this point the air flow and salt-bath temperature were increased to sublime all the products from the top of the catalyst tube and its discharge arm into the air condenser tube. An attempt was made to keep the air rate, time, and temperature of sublimation constant for all runs

so that the quantities of product collected would be truly comparative.

The solid product collected in the air condenser, which usually consisted of beautifully formed white or slightly discolored needles, was scraped out and weighed directly. Homogeneously ground samples were analyzed for phthalic anhydride, corrected for quinone content; the presence of any insoluble matter was noted simultaneously. All material adhering to the inside of the air condenser was washed out with hot water, as were the cold trap and Cottrell precipitator. Any oils in these combined washes were separated by adsorption in activated charcoal powder (Nuchar), and the filtered liquor was analyzed for phthalic anhydride, with quinone corrections. The oil was recovered for separate examination. In some special cases where pure yellow needles of quinone separated on cooling the hot wash, they were filtered out and weighed after drying.

Even with this care possible errors crept into several of the runs. Occasionally small leaks were discovered around the plugs for the air condenser. At higher space velocities the Cottrell precipitator failed to remove all the unreacted hydrocarbon from the exhaust gas. At all times small amounts of products escaped the Cottrell precipitator in true vapor form, not subject to electrostatic precipitation. The aftersublimation procedure was not entirely foolproof.

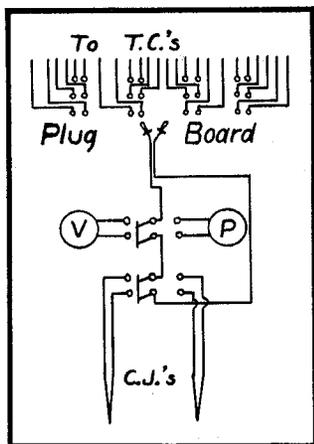


Figure 5. Downs Oxidizer Thermocouple Circuit

Table IV gives an over-all summary of these runs. The space velocity recorded was calculated as liters of entering air per liter of catalyst per hour, corrected to 0° C. and 760 mm., where the air rate is the arithmetic average of meter readings. The catalyst temperature listed is the arithmetic average of the readings of the single thermocouple buried in the catalyst when these readings were steady through the run. Whenever this temperature was variable, the recorded average was obtained by plotting temperature against time and dividing the area under the curve by the total time to give a "graphically integrated" average temperature.

The air-hydrocarbon ratio (air/hc.) was obtained by dividing the total weight of air passed through the vaporizer during actual vaporization of hydrocarbon by the weight of hydrocarbon vaporized.

The weights of products recorded include both the total solid collected directly and the material found by quinone and anhydride analyses of the aqueous washes. No recovered oils are included in these figures. The molecular percentage

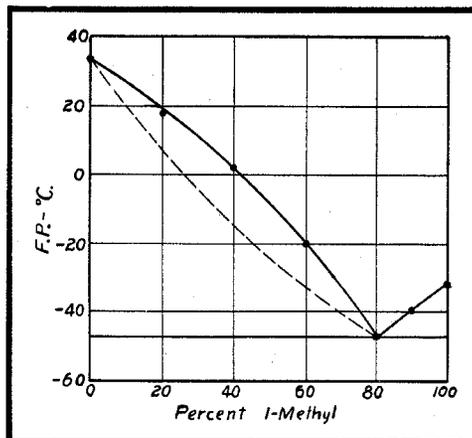


Figure 6. Freezing Points of the System 1- and 2-Methylnaphthalenes

yield of phthalic anhydride is based on the total found by titration of samples of the solids and washes.

The maximum quinone found in solid air-condenser products was 5 per cent or less for both Tetralin and the methylnaphthalenes. This does not correspond necessarily to maximum formation of that material, for at higher space velocity a larger proportion of it passed through to the trap and Cottrell precipitator. Quinones were present to some extent in all products.

Oily products containing unattacked hydrocarbon, a change in catalyst color from the normal orange to a dark greenish or blue-black, and erratic temperature behavior of the catalyst all were correlated with space velocity ranges above 6000.

During the oxidation of methylnaphthalenes the air-condenser solids usually were quinone yellowish during the early part of the runs, but this was superseded by a pinkish to purple cast with tar formation as the runs proceeded. This type of discoloration was evident in all these runs at some point in the condensing system, often imparting that hue to the wash waters. Upon standing in air, however, the purple washes usually turned yellow.

Finally, the products from 2-methylnaphthalene were much more tarry and impure than those from Tetralin at corresponding space velocities. But the purity of the phthalic anhydride was seldom below 95 per cent.

By cooling of hot saturated wash liquors, 1,4-naphthoquinone was isolated from the products of oxidation of Tetralin and 1-methylnaphthalene, and was identified by simple and mixed melting points.

#### Tin-Vanadium Catalyst in Downs Reactor

A series of trial runs was made on all the hydrocarbons to be investigated, using new tin-vanadium catalyst. The chief purpose was to test the operability of the apparatus. The mercury jacket was one third full.

Significant data are listed in Table V. These preliminary runs were made with no thermocouples in the catalyst, but a comparison with later runs allowed the average tube exit temperature to be estimated within 25-30° C. from the pressure on the mercury jacket. The condition of the



Table V. Summary of Runs in Downs Reactor with Tin-Vanadium Catalyst

Run No.	Space Velocity	Jacket Pressure, Lb./Sq. In. Gage	Air/Hc. by Wt.	Estd. Exit Temp., ° C.	Hc. Wt., Grams	Product Wt., Grams	Phthalic Anhydride Yield, %
T-1 MMN	3645	20	66	380	50	26	50
T-1 MN <sub>1</sub>	3530	20	50	370-80	36	12	29
T-1 MN <sub>2</sub>	3455	20	55	370-80	50	13.5	26
T-2 MN <sub>2</sub>	3490	20	65	370-80	35	10.2	30
T-1 T	3550	0	35	310-20	40	24	54

Run No.	Space Velocity	Exit Temp., ° C.	Air/Hc., by Wt.	Hc. Wt., Grams	Product, Wt., Grams	Phthalic Anhydride Yield, %
1 N			Uncontrolled and incomplete			
2 N	3170	270	27.7	40	27	3
3 N	3220	390	26.4	30	15	39
1 T	3320	412	37	50	10	17
2 T	3220	420	32	70	22	28
3 T	3200	435	32	50	19	34
4 T	3260	528	35.6	30	19	52
1 MN <sub>2</sub>	3300	270	34	40	27	3
2 MN <sub>2</sub>	3300	310	33	40	36	2
3 MN <sub>2</sub>			Uncontrolled			
3 MN <sub>2</sub>	3200	390	42	30	8.4	27
4 MN <sub>2</sub>	3140	420	22.5	45	4.0	8.5
5 MN <sub>2</sub>			Uncontrolled			
5, 6, 7 MN <sub>2</sub>			Diluted catalyst, uncontrolled			
1 MN <sub>2</sub> A			Diluted catalyst, alcohol at start, uncontrolled			

catalyst upon removal suggested that there had been some violent departures from this average.

The products were not analyzed; the yields reported are the crude, fairly clean needles from the air condensing system.

In the 2-methylnaphthalene runs a strong, sharp odor of formaldehyde was noticed in the exhaust gas. Tests on brown aqueous condensates and by absorption of some of the exhaust in aqueous-alcoholic sodium bisulfite solution, a test reagent for lower aldehydes (22), resulted in copious precipitation of shiny, white plate crystals.

Esterification of a mixture of the solid products from all these runs with anhydrous ethanol in the presence of a little concentrated sulfuric acid gave an oily product which was vacuum-rectified to yield pure diethyl phthalate (checked by density and index of refraction). All losses except column holdup in the rectification were such as to be proportionate for any mixture of esters possibly present. The holdup was less than 10 per cent of the charge and could have contained no esters more volatile than the main product. Since nowhere were other than characteristic phthalic anhydride needles observed in any solid oxidation products from methylnaphthalenes, and since alkaline titration of these products usually checked out as phthalic anhydride, it is extremely unlikely that the esters of either 1- or 2-naphthoic acids were present in the holdup. These are the only possible acid products of the oxidation of methylnaphthalenes having ethyl esters less volatile than diethyl phthalate. Hence, the only acidic product formed in appreciable amount from the oxidation of methylnaphthalenes is phthalic anhydride.

A second series (MN<sub>2</sub>) was run in the Downs reactor with fresh tin-vanadium catalyst (Table V). Considerable control trouble was experienced in later runs after the catalyst had been overheated by poorly controlled reactions. Table VI shows the nature of the products from this series.

### Vanadium Pentoxide on Silica Gel in Downs Reactor

The exit temperatures (Table VII) are integrated averages for the sheathed thermocouple buried in the exit layer of catalyst. The entering temperatures are integrated averages of the bare thermocouple surrounded by the entering layer of catalyst. Figure 7 is an example of the record of these thermocouples used to obtain integrated averages. Space velocity and air/hydrocarbon ratio are defined as before. The weights of product include crude solids and wash liquor contents. The solid products from runs on methylnaphthalenes contained a deep purple discoloration which was very soluble in water. The mercury jacket was two thirds full in this series.

During runs 1 and 2 MN<sub>2</sub>L an attempt was made to hold the space velocity at 4100-4200. The catalyst temperature went wild again, temperatures as high as 1100° C. being observed. The reaction was explosive and produced soot at these high temperatures. The catalyst was ruined (fused to a blue, glassy material). No solid oxidation products were obtained.

Fresh catalyst was used in the subsequent runs. Lowering the vaporizer temperature from 140° to 130° C. seemed to bring the reaction into a controllable productive range. The trouble with those first two runs was probably caused by insufficient air, which placed the mixture in the explosive range and failed to dilute the heat effect sufficiently.

The water-scrubbing column was substituted for the Cottrell precipitator throughout this series.

The yellow liquor from the column and washing liquors from run 2 NL were adjusted to 1 liter in volume and extracted continuously for 6 hours with 100 ml. of benzene.

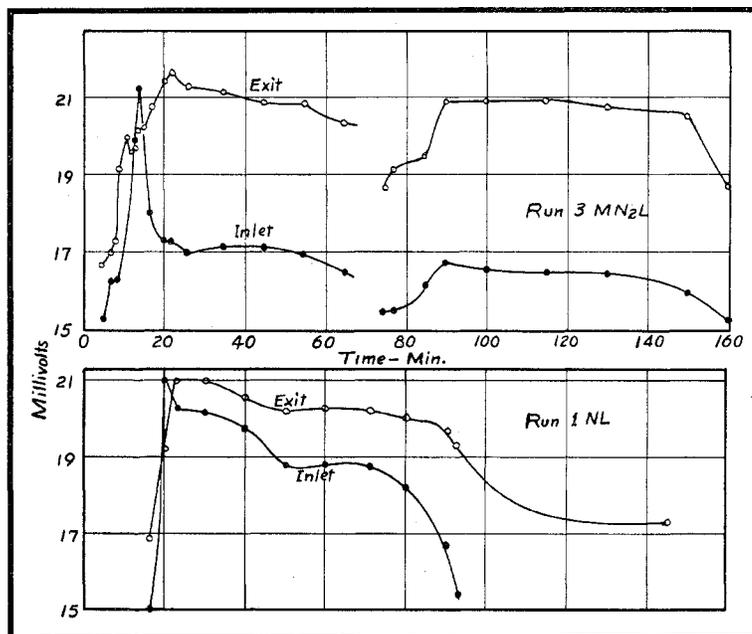


Figure 7. Typical Records of the Catalyst Thermocouples in the Laboratory Downs Oxidizer

Table VI. Account of Materials Based on Analysis of Tin-Vanadium Runs in Downs Reactor

Run No.	Phthalic Anhydride Yield, %	Quinone Yield, %	Hc. Recovered as Such, %	Hc. Lost, %
2 N	3	3	58	36
3 N	39	4	8	49
1 T	17	3	..	80
2 T	28	1	..	71
3 T	34	1	..	65
4 T	52	3	1	44
1 MN <sub>2</sub>	3	2	64	31
2 MN <sub>2</sub>	2	6	82	10
3 MN <sub>2</sub>	27	..	..	73
4 MN <sub>2</sub>	8.5	..	..	91.5

The yellow benzene extract was stripped of solvent and dried, and the residue sublimed at 100° C. and 5 mm. pressure to give an orange, semicrystalline condensate. The solid was recrystallized quantitatively from aqueous alcohol to give 0.25 gram of yellow needles which melted at 124-126° C. (corrected). This product was 1,4-naphthoquinone.

The procedure proved capable of isolating quinone from the washes. The process was repeated on the wash liquors from runs 3, 4, and 5 MN<sub>2</sub>L. Sublimation of the combined benzene residues gave an oily, orange, semiliquid condensate, similar to that from the naphthalene product except that it was more liquid. Attempts to recrystallize an identifiable solid failed.

Table VII. Summary of Runs in Downs Reactor with V<sub>2</sub>O<sub>5</sub> on Silica Gel Catalyst

Run No.	Space Velocity	Inlet Temp., ° C.	Exit Temp., ° C.	Air/Hc. by Wt.	Hc. Wt. Grams	Product Wt. Grams	Phthalic Anhydride Yield, %
1 TL	4160	456	460	16	80	58	65
2 TL	7030	388	475	30	40	32	72
1 NL	4080	462	480	11	60	53	76
2 NL	6860	370	473	28	40	33	72
3 NL	4180	443	480	13	60	43	63
1 MN <sub>2</sub> L				Uncontrollable			
2 MN <sub>2</sub> L				Uncontrollable			
3 MN <sub>2</sub> L	4180	402	490	23	60	31	50
4 MN <sub>2</sub> L	4160	420	485	21	50	27	52
5 MN <sub>2</sub> L	6980	351	530	40	40	21	51

The crude sublimates from the naphthalene and 2-methylnaphthalene quinone processing were compared. While the naphthalene product was mostly 1,4-naphthoquinone, with perhaps a little phthalic anhydride to lower its melting point, the condensate from the 2-methylnaphthalene product (much more liquid in character) admitted the possibility of a chemically and physically inseparable mixture of 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone as well as traces of phthalic anhydride.

### Yields

**CURVES.** Figure 8 shows roughly the relation between molecular percentage yield of phthalic anhydride and space velocity for the temperatures and air/hydrocarbon ratios indicated. These curves are based on runs in the glass reactor with pure vanadium pentoxide catalyst. Since errors in technique could not be entirely avoided, only the runs having the highest yield for a given space-velocity range are plotted. This selection of points probably gives a true picture of the shape and trend of these curves.

Failure of the points to fall exactly on a smooth curve may also be explained partially by the fact that it proved imprac-

tical to maintain identical air/hydrocarbon ratios and catalyst temperature throughout a long series of runs where other variables were not to be held constant. The direction of probable yield correction for individual points to eliminate technical errors and reduce all points to the indicated standard temperature and air/hydrocarbon ratio is shown by arrows originating in some of the points.

These corrections are based on the following reasonable assumptions: (a) Technical errors were usually the result of material loss in collecting and handling the products. (b) Air/hydrocarbon ratio and temperature higher than the standard caused a lowered yield, within small ranges of these variables, resulting from a greater degree of complete combustion. The reverse of (b) may be true at higher space velocities where an increase in these factors may result in an increase in yield, due to more complete attack on the hydrocarbon which would have remained untouched at the standard condition chosen (4, 5, 12).

These yield-space velocity curves show the expected form. At low space velocities the losses are caused by complete combustion of the product; at higher space velocities hydrocarbon may come through unattacked. A maximum yield is found between these extremes. This is a general characteristic of catalytic vapor-phase oxidations (19).

**MAXIMUM YIELDS.** That the maxima exhibited in the yield-space velocity curves should shift along the space velocity axis with changes in temperature is to be expected, because high space velocity (low contact time) should be necessary to produce the same extent of reaction at higher temperature where reaction velocity is higher. The principle of increase in reaction velocity with temperature is quite general, because the effect of increased temperature is the activation of a greater proportion of the participating molecules per unit time to an adequate energy level for reaction.

Figure 8 gives evidence of this shift, although the difference between the temperatures chosen appears insufficient to indicate a marked variation.

Examination of the maxima (Figure 8 and Table VII) shows that naphthalene and Tetralin gave comparable yields which, moreover, were 1.4 to 1.7 times as high as the yields from methylnaphthalenes. Probable pyrolysis of the methylnaphthalenes may be indicated from this fact about the comparative yields and from the apparently greater complexity of the products of the methylnaphthalenes; also purely pyrolytic studies (3, 14, 15, 23) show that, in the temperature range of the present study, both naphthalene and Tetralin are relatively stable to heat whereas the methylnaphthalenes are somewhat decomposed.

**COMPARISON WITH PREVIOUS WORK.** Table VIII summarizes most of the material found in the literature which gave experimental data on yields and conditions.

### Behavior of Catalyst

This investigation is the first recorded in which the catalyst has been observed while the reaction was in progress. Visual evidence thus has been added in support of the theory of oxidation-reduction equilibria in the operation of the vanadium pentoxide catalyst. Changes in the surface state of the catalyst also were obvious (19).

Weiss, Downs, and Burns (25) first established the existence of a



Table VIII. Comparison of Yields with Previous Work

Hydrocarbon	Phthalic Anhydride Yield, %	Temp., ° C.	Space Velocity	Catalyst	Scale of Operation	Reference
C <sub>10</sub> H <sub>8</sub>	80	...	...	...	Laboratory	(8, 11)
	84	280	...	Sn-V	Laboratory	(20)
	66	370	470	V <sub>2</sub> O <sub>5</sub>	Laboratory	(12)
	61	290	...	Sn-V	Laboratory	(6)
	69 <sup>a</sup>	...	...	V <sub>2</sub> O <sub>5</sub>	Commercial	(10, 13)
	76	460-80	4060	V <sub>2</sub> O <sub>5</sub>	Downs reactor	Table VII
C <sub>10</sub> H <sub>12</sub>	53	...	...	Sn-V	Laboratory	(20) 4 runs
	67	320-60	470	V <sub>2</sub> O <sub>5</sub>	Laboratory	(12) 8 runs
	70	440	3780	V <sub>2</sub> O <sub>5</sub>	Glass reactor	Table IV
	72	400-75	7030	V <sub>2</sub> O <sub>5</sub>	Downs reactor	Table VII
MeC <sub>10</sub> H <sub>7</sub>	43	465	4120	V <sub>2</sub> O <sub>5</sub>	Glass reactor	Table IV
	52	420-85	4160	V <sub>2</sub> O <sub>5</sub>	Downs reactor	Table VII

<sup>a</sup> 80 pounds per 100 pounds.

variable V<sub>2</sub>O<sub>4</sub>/V<sub>2</sub>O<sub>5</sub> ratio in the normal catalyst by quantitative analysis of the catalyst, both before and after oxidations of benzene at varying air/hydrocarbon ratios.

Qualitative observations of the variation of catalyst color in the present investigation indicated that space velocity alone, at constant temperature and air/hydrocarbon ratio, had a pronounced effect on the composition of the catalyst. At space velocities above 6000 in the glass reactor the catalyst was in a reduced state which was undesirable catalytically and led to poor control of the reaction and incomplete attack on the hydrocarbon. The catalyst could be returned readily to an active state by brief aeration at the reaction temperature.

Furthermore, the active catalyst surface was not the original fused macrocrystalline vanadium pentoxide which was charged in new catalyst. Comparison of the orange color of the catalyst after use with the purple-red crystalline nature of fresh catalyst suggested that the active material is in either a microcrystalline or amorphous finely divided state similar to vanadium pentoxide prepared by rapid precipitation of fine, orange vanadic acid in aqueous medium. Accompanying this change in surface state, there would necessarily be an enormous increase in the contact area of the surface. It was likewise noticed that the catalyst was inactive after fusion in the presence of the reaction mixture and that it could not be reactivated readily from this state.

Observations on the tin-bearing catalyst were limited and inconclusive. However, the fact that the initiating temperature range of this catalyst for partial oxidation, once it had been fused in the reactor (500-600° C.), was in the range for the start of noncatalytic oxidation suggested that, by fusion or reduction or both, the catalyst had become an inert material for practical purposes.

Some of the more successful tin-bearing catalysts previously reported were prepared from stannic chloride rather than from stannous chloride dihydrate as tried here. If the latter is the reason for the poor stability of the catalyst discussed, it cannot be rationalized when the treatment accorded these catalysts in the reactor tube is considered; stannous chloride and stannic chloride would both be expected to yield stannic oxide as the result of treatment at high temperature with air containing some water vapor.

### Estimation of Heat Transfer Coefficients in Catalyst Tube

The average temperature difference between catalyst and mercury jacket may be used to estimate the magnitude of the effective over-all heat-transfer coefficient in the catalyst tube.

A simple heat balance can be written about the tube, assuming that the only heat losses of the tube are to the bath and in the heat content of the exit gases above the entering catalyst temperature. Other small effects, such as preheating the gases from 250-300° C. to the entering catalyst temperature by the condensation of mercury vapor on the upper third of the catalyst tube, and such as proportionately small increases in the number of moles of gas leaving over that entering due to the production of carbon dioxide and water vapor, will be ignored. Actually, a material balance shows that the maximum molal increase of the gases possible (by complete combustion of methylnaphthalene at theoretical air ratio) is only about 4.5 per cent. Actual conditions with more than theoretical air and large formation of partial oxidation products minimizes this error.

Table IX. Summary of Hydrocarbon Reactions

Hydrocarbon	Reaction	Theoretical Air/Hc. by Wt.	Gram-cal./Mole at 450° C.
C <sub>10</sub> H <sub>8</sub>	Complete combustion	13.0	Q <sub>c</sub> = 1,207,000
	To phthalic anhydride	4.84	Q <sub>pa</sub> = 416,100
C <sub>10</sub> H <sub>12</sub>	Complete combustion	13.6	Q <sub>c</sub> = 1,306,000
	To phthalic anhydride	5.75	Q <sub>pa</sub> = 501,400
MeC <sub>10</sub> H <sub>7</sub>	Complete combustion	13.1	Q <sub>c</sub> = 1,357,000
	To phthalic anhydride	5.83	Q <sub>pa</sub> = 555,100

Such a rough heat balance, based on the law of conservation of energy, for the steady state of both heat and material flow may be expressed as in Equation 1.

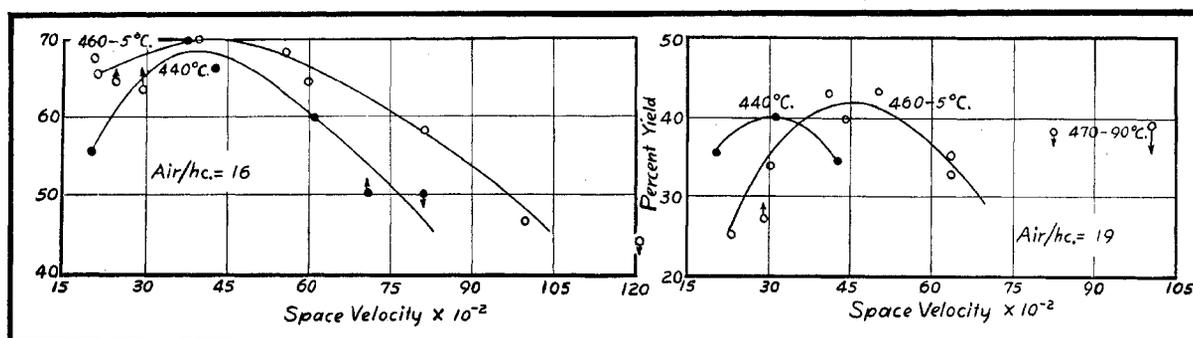


Figure 8. Yield of Phthalic Anhydride from Tetralin (left) and from 2-Methylnaphthalene (right)

Table X. Computation of the Heat Transfer Equation

[Volume of catalyst = 100 cc.;  $A = 146$  sq. cm.;  $c_p = 0.25$  cal./gram)(°C.)]

Run No.	Space Velocity	Temperature, °C.		Yield Phthalic Anhydride, %	Ratio Air/Hc.	$M$	$Q_r$	$\frac{Q_r}{RM}$	$T_{ex} - T_{in}$	$c_p \Delta T$	$\frac{Q_r}{RM - c_p \Delta T}$	$T_c - T_b$	$\frac{0.000887 SV}{T_c - T_b}$	$U^*$ Gram-cal. (Sq. Cm.)/ (Hr.)(°C.)
		Exit	Inlet											
1 TL	4160	460	456	398	65	132	786,500	373.0	4	1.0	372.0	60	0.0615	22.9
2 TL	7030	475	388	400	72	132	726,800	163.5	87	22.0	141.5	31	0.201	28.5
1 NL	4060	480	462	386	76	11	604,000	429.0	18	4.5	424.5	85	0.0423	17.9
2 NL	6860	473	370	395	72	28	641,000	176.5	103	25.8	150.7	26	0.234	35.2
3 NL	4180	470	442	404	63	13	711,500	421.5	27	6.8	414.7	53	0.070	29.0
3 MN <sub>2</sub> L	4180	490	402	406	50	23	956,000	299.0	88	22.0	277.0	40	0.093	25.8
4 MN <sub>2</sub> L	4160	485	420	408	52	21	942,500	310.0	65	16.3	293.7	46	0.0802	23.6
5 MN <sub>2</sub> L	6960	530	351	406	51	40	947,700	166.7	179	45.0	121.7	35	0.177	21.5

\* To convert to B.t.u./(sq. ft.)(hr.)(° F.), multiply by 2.05.

$$w c_p (T_{ex} - T_{in}) + UA(T_c - T_b) = \frac{w Q_r}{RM} \quad (1)$$

$$\left[ \begin{array}{l} \text{heat in gases leaving} \\ \text{above entering cata-} \\ \text{lyst temp.} \end{array} \right] + \left[ \begin{array}{l} \text{heat lost} \\ \text{through} \\ \text{tube wall} \end{array} \right] = \left[ \begin{array}{l} \text{total heat liber-} \\ \text{ated by actual} \\ \text{reaction} \end{array} \right]$$

where  $w$  = weight of air, grams/hr.  
 $c_p$  = gram-specific heat of air at 400–500° C.  
 $U$  = over-all heat transfer coefficient, gram-cal. (sq. cm.)(hr.)(° C.)  
 $A$  = inside tube-wall area in contact with catalyst, sq. cm.  
 $R$  = air/hydrocarbon ratio by weight  
 $M$  = mol. weight of hydrocarbon  
 $(T_{ex} - T_{in})$  = av. temp. difference between ends of catalyst mass  
 $(T_c - T_b)$  = arithmetic av. catalyst temp. minus bath temp.  $[(T_{ex} - T_b) + (T_{in} - T_b)]/2$   
 $Q_r$  = heat liberated per mole hydrocarbon reacted, gram-cal.

 $Q_r$  is defined by Equation 2:

$$Q_r = \left( \frac{Y}{100} \right) (Q_{pa}) + \left( \frac{(100 - Y)}{100} \right) (Q_c) \quad (2)$$

where  $Y$  = yield of phthalic anhydride, mol. %  
 $Q_{pa}$  = heat of reaction to phthalic anhydride  
 $Q_c$  = heat of complete combustion

The small heat effect in the formation of small amounts of quinones and other products is neglected.

Solving Equation 1 gives Equation 3:

$$U = \left( \frac{w}{A(T_c - T_b)} \right) \left[ \left( \frac{Q_r}{RM} \right) - c_p (T_{ex} - T_{in}) \right] \quad (3)$$

It is useful to convert  $w$  into terms of space velocity,  $SV$ , which was calculated at standard conditions of temperature and pressure:

$$w = \frac{(29 \text{ g./mole}) (SV \text{ l./hr./l. of catalyst}) (0.1 \text{ l. of catalyst})}{22.4 \text{ l./mole}}$$

Inserting this value and the tube-wall area,  $A = 146$  sq. cm., into Equation 3, and solving gives the final form:

$$U = \left( \frac{0.000887 SV}{(T_c - T_b)} \right) \left[ \left( \frac{Q_r}{RM} \right) - c_p (T_{ex} - T_{in}) \right] \quad (4)$$

For estimation of  $Q_r$  a survey of the reactions involved with their heat effects at 450° C. is necessary (rough calculations made from known or accurately estimated heats of reaction at 20° C.). Table IX indicates this information. Since the heat effects were not based on complete thermodynamic data, their absolute accuracy may be doubtful; but their comparative

values serve adequately for this rough study which is designed primarily to indicate a possible method of attack on the problem of heat transfer in these catalyst tubes.

The data and calculations for solving Equation 4 are summarized in Table X. The limited data and lack of precision in control and measurements here probably make the values of  $U$  only approximate. However, with refined calorimetric technique and more extensive data, application of this method of attack will lead to results of both practical and theoretical interest.

### Conclusions

1. Naphthalene, Tetralin, and the methylnaphthalenes are oxidized catalytically in the vapor phase to phthalic anhydride as the chief stable partial oxidation product.

2. Methylnaphthalenes produce lower yields of phthalic anhydride than naphthalene and Tetralin under the same conditions.

3. If yield of phthalic anhydride is plotted against space velocity (temperature and air/hydrocarbon ratio constant), the curve for 2-methylnaphthalene shows the same form as that for Tetralin; both curves are of the type usually associated with catalytic vapor-phase oxidations.

4. At space velocities higher than that for maximum yield of phthalic anhydride, darkening or reduction of the catalyst, incomplete attack on the hydrocarbon, and erratic behavior of the catalyst temperature set in gradually and become progressively worse, the higher the space velocity.

5. The simplest preparation of an effective catalyst is afforded by fusion of pure vanadium pentoxide onto a suitable carrier, of which silica gel is a good example.

6. Stannous chloride may not be a satisfactory intermediate for the preparation of the tin vanadate type catalysts.

7. Catalysts may become inactivated by overheating or excessive reduction or both. If the conditions of this destruction of activity are not too severe, the catalyst can be reactivated by aeration at the reaction temperatures.

8. Inactivated catalysts give incomplete attack at excessive temperatures to form difficultly condensable and non-uniform products.

9. A heat balance over the catalyst tube, based on simple temperature and flow measurements, serves to establish the general magnitude of the effective over-all heat transfer coefficient of the catalyst tube; it is, in effect, a packed tube operating at high temperature under the influence of a thermochemical reaction. A method of attack is indicated for problems of this type.

