Nomenclature

B = volume of liquid on tube wall
C = volume of liquid clinging per sq. cm. of surface
f = Fanning friction factor, $2\,gm^3/Q^2$
g = acceleration of gravity, 981 cm./(sec.) (sec.)
ΔH = increase in height of liquid level
m = film thickness, cm.
Q = volumetric discharge per unit of periphery, cc./cm./sec.
R = inside radius of outer tube
r = outside radius of inner tube
Re = Reynolds number, $4Q\rho/\mu$
U = velocity of liquid film at liquid-gas interface, cm./sec.
V = average velocity of liquid film, cm./sec.
v = velocity in film at distance x from tube wall
ρ = density of film liquid, grams/cc.
μ = absolute viscosity of film liquid, poises

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Vapor-Phase Catalytic Oxidation of Organic Compounds

Production of Benzoic Acid, Maleic Acid, and Benzaldehyde from Toluene at Atmospheric Pressure[1]

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The direct vapor-phase catalytic oxidation of toluene in the presence of various solid catalysts to produce benzaldehyde and benzoic acid has been investigated. Vanadium pentoxide prepared by the decomposition of ammonium metavanadate at temperatures below 300° C. was the most satisfactory catalyst. The effect of temperature, time of contact, air/toluene ratio and concentration of vanadium pentoxide on Alfrax, granular aluminum, and silica gel was measured.

The highest yields of partial oxidation products were obtained with vanadium pentoxide supported on Alfrax at temperatures between 380° and 460° C., time of contact 0.5 second, and air/toluene ratio above 25. Under these conditions the maximum yield of benzoic acid, maleic acid, and benzaldehyde was 34, 21, and 12 per cent, respectively. Although the mechanism for the formation of maleic acid is complex, relatively large quantities were produced. The results indicate that the most important variables controlling this reaction are temperature and method of catalyst preparation.

ALTHOUGH the direct vapor-phase catalytic partial oxidation of toluene presents some difficulties, the possibility of commercial operation of some process is attractive because of the high ratio between raw material cost and value of the products free from chlorine and other inorganic impurities. The desirable products of toluene oxidation are mainly benzaldehyde, benzoic acid, and anthraquinone. They are obtained in proportions that depend upon catalyst, temperature, oxygen ratio, and time of contact. The formation of benzaldehyde is favored by a high temperature, mild catalyst, and short time of contact. With a high oxygen-hydrocarbon ratio and long time of contact the principal product is benzoic acid. In the presence of vanadium oxide catalysts the oxidation reaction begins at approximately 300° C. However, the most favorable temperature is somewhat higher, 400–450° C., where approximately 50 per cent of the toluene oxidized per pass forms benzaldehyde. Molybdenum oxide is a less active catalyst and requires a higher temperature for high per-pass yields. With a tin vanadate catalyst at 290° C., 53 per cent of the toluene oxidized per pass forms benzoic acid (*12*). Anthraquinone may be formed (< 5 per cent) under certain conditions, but it is of no economic importance.

A great deal of information on catalysts, construction of apparatus, and conditions for operation is to be found in the literature and in the numerous patents issued following the investigations of Gibbs (*3*) and Weiss and Downs (*17*). In the vapor-phase oxidation of toluene by air, complete combustion occurs with cobalt and cerium oxides, while manganese, copper, nickel, chromium, and uranium are less active. Vanadium oxide occupies an intermediate position and produces

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[1] The first two papers in this series appeared in 1936 (*16*) and 1939 (*14*).
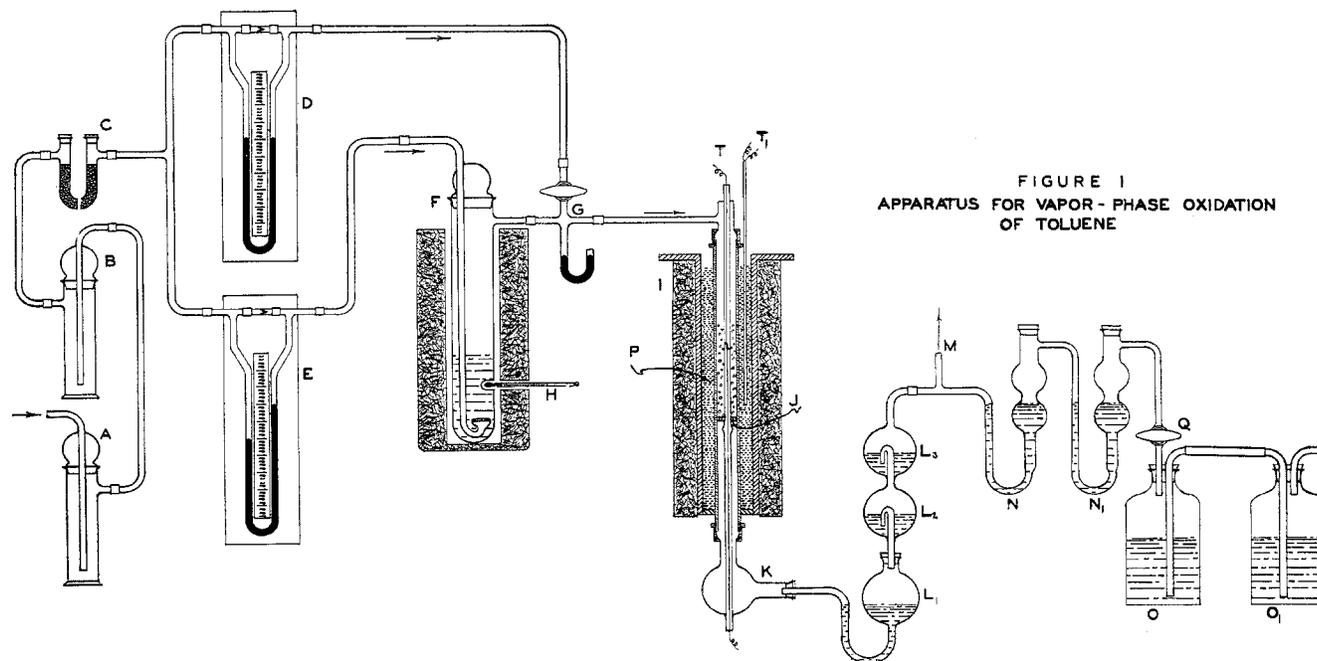
FIGURE 1

APPARATUS FOR VAPOR-PHASE OXIDATION
OF TOLUENE

favorable yields of benzoic acid. Molybdenum, tungsten, and zirconium oxides favor the formation of benzaldehyde. Most other oxides have very little catalytic action, and the dependence of the effect on the position in the Periodic Table is apparent (11). In the formation of benzoic acid the temperature and oxygen concentration influence the ratio of carbon dioxide to benzoic acid, but diluents such as carbon dioxide and water vapor appear to have no influence on the reaction. The effect of such factors as the chemical nature and physical structure of the catalyst, method of preparation, support, time of contact, temperature, composition of gaseous mixture, and extent of surface and amount of catalyst has been studied extensively (1, 6, 9, 14, 15, 18). The amount of organic vapor consumed in complete combustion is independent, over a considerable range, of the time of contact and concentration. The quantity and nature of the catalyst are most important. The ratio of partial to total oxidation products is independent of the rate of flow.

The object of this investigation was to determine the catalytic activity of various compounds in the partial oxidation of toluene to either benzaldehyde or benzoic acid with varying temperature, air-hydrocarbon ratio, time of contact, and catalyst support at atmospheric pressure. Several metal vanadates, such as tin, vanadium, and bismuth, were known to have considerable activity in this reaction (6). However, after such compounds as uranium, iron, copper, calcium, zinc, silver, and cerium vanadate were used with unsatisfactory results, a thorough investigation of the activity of various samples of vanadium pentoxide on different supports was undertaken. Measurements were made on all materials introduced into the reactor.

Experimental Procedure

The apparatus is shown in Figure 1. Air from a compressor (tank pressure 40 pounds per square inch) after passing through a diaphragm reducing valve (5 pounds per square inch low pressure outlet) was purified by sulfuric acid, A, potassium hydroxide, B, and anhydrous calcium sulfate, C. After purification the air stream was divided into two parts and metered through two calibrated flowmeters containing dibutyl phthalate (5) colored

red by a small quantity of Sudan III. The primary air passed through flowmeter E into toluene vaporizer F where a sintered glass disk produced small bubbles to facilitate saturation. The vaporizer was enclosed in an electrically heated Alundum tube. The quantity of toluene vaporized was controlled by varying either the primary air flow or the temperature of the vaporizer, measured by thermometer H. The hydrocarbon-air mixture was joined at G by the secondary air metered by flowmeter D. The reaction mixture passed into reactor I containing the catalyst and then through the condensing system and gas sampling apparatus.

The reactor consisted of a half-inch (1.3-cm.) i. d. calorized steel tube, 24 inches (61 cm.) long, extending through the longitudinal axis of 3-inch (7.6-cm.) standard iron pipe 17 inches (43.2 cm.) long. The 3-inch pipe was closed at the bottom, and the smaller tube passed through the center. The larger tube served as the salt bath, P, containing a mixture of 45 per cent sodium nitrate and 55 per cent potassium nitrate (12). An electric heating unit was wound around the outside of the 3-inch pipe and insulated with asbestos paper. A sufficiently constant temperature was maintained (Figure 2) without agitation of the nitrate bath. The reactor was mounted in a vertical position with the gases passing down through the catalyst layer. A piece of 3-mm. Pyrex tubing extended through the center of the catalyst tube and projected from each end. The catalyst layer was packed around the Pyrex tube supported by a perforated porcelain disk, J, inserted 6 inches (15 cm.) from the lower end of the calorized tube. Catalyst temperatures were measured by thermocouple T with a lead coming out of each end of the Pyrex tube. The junction of the thermocouple could be moved throughout the length of the catalyst mass. Another thermocouple, T_1, was inserted into the salt bath and could be moved to any point in the bath. The temperature of the reactor and vaporizer was controlled by variable resistances not shown on Figure 1. The efficiency of the reactor in removing the heat of reaction was tested by oxidizing naphthalene to phthalic anhydride with a vanadium oxide catalyst. Satisfactory temperature control is more a function of total than of partial oxidation. The heat evolved in the oxidation of a mole of naphthalene to phthalic anhydride is in excess of that produced in oxidizing a mole of toluene to benzaldehyde or benzoic acid. However, in oxidizing toluene, the evolution of heat due to the reaction to aldehyde or acid is only a part of the total heat liberated, because under the conditions some toluene is burned to carbon dioxide and water and the heat thus produced is approximately six times that due to the formation of benzoic acid.

The condensing system consisted of an air condenser, K, followed by three scrubbers, L_1, L_2, L_3, in which various liquids (95 per cent ethyl alcohol, toluene, and water) were used as

solvents. The gas sampling unit consisted of two scrubbers, the first, N, containing alcohol and the second, N_1, water. The exit gases were drawn through these scrubbers into a large bottle, O, filled with a 10 per cent sodium sulfate solution. The flow of the continuous gas sample was induced by siphoning the sodium sulfate solution into another bottle, O_1. The rate of flow was controlled by stopcock Q, and by a pinch clamp not shown on the tubing connecting the two bottles. The pressure was equalized at M when necessary. A representative sample of the exit gases was collected during at least one third of the run after sufficient time had been allowed for the air in the condensing system and sampling bottle to be displaced. Hundred-milliliter portions of this gas sample were analyzed for carbon dioxide, carbon monoxide, and oxygen.

The conditions (temperature, air/toluene ratio, and time of contact) were established for each experiment, and the correct quantities of air and toluene were calculated. From the experimental vaporizer curves, the quantity of primary air necessary to vaporize the required amount of toluene was determined, and any additional air required was supplied as secondary air. The amount of toluene passed through the apparatus was determined by weighing the vaporizer before and after each run. In all runs at least 2 grams of toluene were used in order to obtain a precision better than 2 per cent. The secondary air was blown through the apparatus for 5 minutes before each run was started and, after the primary air was turned off at the end of the run, was continued until the catalyst temperature had dropped to the salt bath temperature.

The method of analyzing the condensate was varied to accommodate the yield of partial oxidation products and to simplify the work. If benzaldehyde and total acid alone were determined, the condensers and scrubbers were washed with a 50 per cent (by volume) solution of toluene in ethyl alcohol. The wash solution was added to the condensate and diluted to 250 ml. in a volumetric flask. The total acidity was determined by titrating a 25-ml. aliquot to which 25 ml. of ethyl alcohol were added with 0.1 N sodium hydroxide to a red end point, using 3 ml. of a 0.02 per cent solution of phenol red in ethyl alcohol as the indicator. In the early experiments no attempt was made to distinguish between maleic and benzoic acid. To determine benzaldehyde, 10 ml. of a 5 per cent solution of sodium bisulfite were added to a 10-ml. aliquot in a 250-ml. flask. The flask was stoppered immediately and kept in an ice bath for at least an hour with frequent shaking. The excess bisulfite was then titrated with 0.2 N iodine, using a starch indicator. The iodine was added rapidly until near the end point and then dropwise to a blue color lasting for at least 20 seconds. A blank was run along with the sample, using 10 ml. of the 50 per cent toluene in ethyl alcohol solution and 10 ml. of the bisulfite solution. If anthraquinone was to be determined, 95 per cent ethyl alcohol was used as the wash solution. Since anthraquinone is only slightly soluble in alcohol, the crystals were removed by filtration and weighed directly. Alcohol interferes with the iodine end point, so that the benzaldehyde analysis was modified by adding 50 ml. of ice water before the excess bisulfite was titrated. If maleic acid was determined, pure toluene was used in the scrubbers and as a wash solution. Maleic acid is insoluble in toluene and may be separated by filtration. The condensers and filter paper were washed with hot water. The toluene solution was analyzed for benzoic acid and benzaldehyde. The water solution was analyzed for maleic acid by titrating a 100-ml. sample with 0.5 N sodium hydroxide, using bromothymol blue as the indicator.

Preparation of Catalysts

The vanadium catalysts were prepared by the decomposition of ammonium metavanadate on various supports in an electrically heated calorized steel tube. A measured quantity of air was passed through the tube during the reaction. In the preparation of catalyst 1, containing 12 per cent V_xO_y on silica gel (10), 24.6 grams of silica gel, 3.6 grams of vanadium pentoxide, 9.1 grams of oxalic acid, and 30 ml. of water were placed in a beaker and evaporated to dryness with constant stirring on a steam bath. The catalyst was transferred to the special reactor at 280° C. and maintained at this temperature for 3 hours. Purified air was passed through the mass at the rate of 11 liters per hour during decomposition. Catalyst 2 was prepared from commercial vanadium pentoxide and Alfrax. The wet paste was evaporated to dryness to distribute the oxide evenly but was not further heated. For catalysts 3 to 8 a weighed quantity of the support (silica gel, granular aluminum, or Alfrax) and the required amount of ammonium metavanadate were placed in a beaker with sufficient water to make a wet paste. The catalyst particles, after drying on a steam bath, were transferred to the reactor tube and decomposed at 300° C. The time of decomposition was

varied from 2 to 16 hours. Eleven liters of air per hour were passed over the catalyst during the decomposition. Catalyst 9 was prepared from 8 by removing sufficient vanadium pentoxide from the Alfrax support. Catalyst 10 was prepared by removing the particles from the tube after decomposition and again adding sufficient water to make a wet paste. After evaporation to dryness on a steam bath the catalyst was heated for 5 hours at 130° C. in an oven. Catalysts 11, 12, and 13 were prepared from 10 by removing the required amount of vanadium pentoxide. For all catalysts 30 ml. of the support (8–14 mesh measured in a graduated cylinder after gentle tapping appeared to produce no further settling) were weighed. The percentage of vanadium pentoxide was calculated on the dry basis.
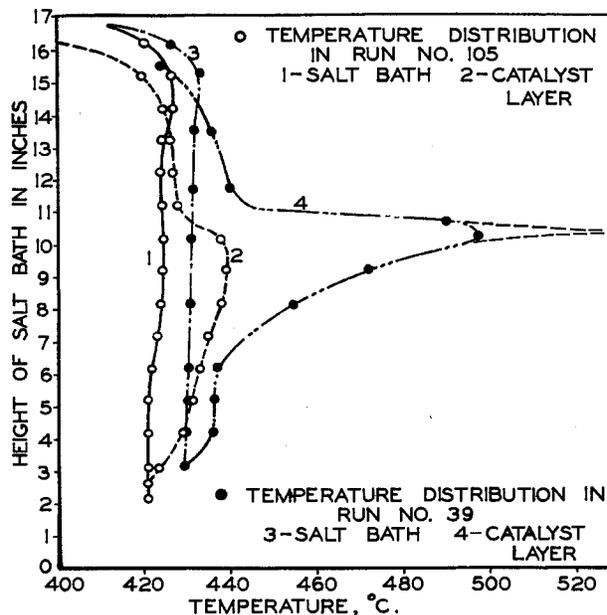
FIGURE 2. TEMPERATURE DISTRIBUTION IN THE OXIDATION OF TOLUENE

Results with Various Catalysts

The data obtained from 251 experiments employing various catalysts under varying conditions are summarized in Table I. The results are expressed on the basis of the toluene vaporized, since none was recovered. Sufficient oxygen was present for complete oxidation which, together with the slight losses involved, accounted for all toluene passed through the reactor. The most important products resulting from the oxidation of toluene at elevated temperatures and atmospheric pressure are benzaldehyde, benzoic acid, maleic acid, and anthraquinone. The reactions to form benzaldehyde and benzoic acid are believed to take place through a hydroxylation mechanism, although benzyl alcohol has never been isolated as a partial oxidation product at atmospheric pressure. However, Newitt and Szegö (13) reported that, at a pressure of 50 atmospheres and a temperature of 210° C., 61 per cent of the toluene oxidized is converted into hydroxylated compounds consisting chiefly of benzyl alcohol and benzoic acid. At atmospheric pressure, oxidation of toluene does not begin until approximately 300° C. with most catalysts. Benzyl alcohol is thermally unstable above 210–215° C. The formation of maleic acid from toluene may be explained as resulting from the oxidation of the benzene produced by the pyrolysis of benzaldehyde or benzoic acid $(7, 8)$. Benzene may also be formed by the decarboxylation of benzoic acid. The mecha-

nism for the formation of anthraquinone (oxidation and condensation of benzaldehyde) was suggested by Downs (2).

The extensive use of air/toluene ratios on the lean side of the explosive range has not been reported in the literature. From a commercial standpoint the per-pass yield is important because the cost of production is increased by the recovery and recirculation of the unreacted toluene. A consideration of the yields obtained with different air/toluene ratios indicates the use of the lean side of the explosive range. The rich limit of the explosive range calculated from volume per cents (16) is an air/toluene ratio of 4. The theoretical air/toluene ratio to benzaldehyde is 1.5, to benzoic acid 2.25,
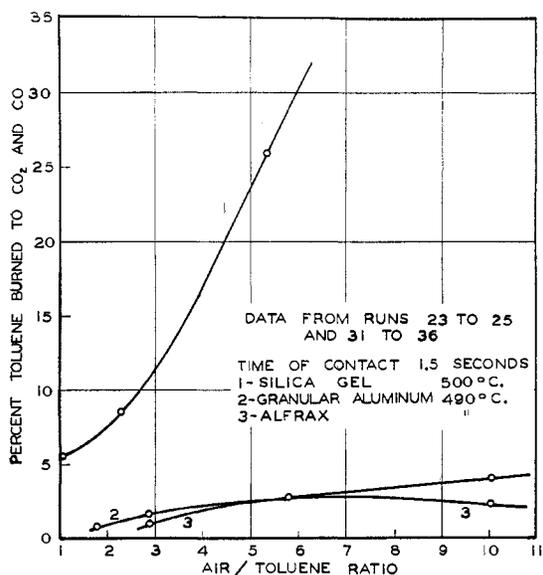
FIGURE 3.   EFFECT OF VARYING THE AIR/TOLUENE
RATIO WITH THREE SUPPORTS

and to carbon dioxide and water 13.5. In order to be safely outside the explosive range, ratios only slightly in excess of the theoretical to benzoic acid may be used. At this ratio it is doubtful whether high per-pass yields can be obtained. To obtain high yields a very selective catalyst would be necessary and would have to be operated under rigidly controlled conditions. With the large quantity of oxygen consumed in the combustion of toluene to carbon dioxide and water, a small amount of toluene completely oxidized would decrease the oxygen concentration so much that a low yield of partial oxidation products would result. The successful commercial reactions, such as naphthalene to phthalic anhydride and benzene to maleic acid, use a large excess of air. Other factors are involved since with toluene it is desired to oxidize mildly an aliphatic side chain to relatively unstable products, whereas in the case of naphthalene and benzene it is necessary to burn a portion of the benzene ring to obtain stable products. Air/toluene ratios on the rich side of the explosive range and with a relatively long time of contact (low space velocity) have been investigated. At low air ratios a short time of contact (0.5 second or less) is difficult to control because the quantity of toluene oxidized per unit volume of catalyst is too large for the heat removal capacity of the converters. Since low air ratios and short times of contact favor aldehyde formation, the most favorable conditions are not easily obtained.

The temperature distribution inside the empty catalyst tube was determined. The measurements indicated that the catalyst occupied a zone of constant temperature at the beginning of the reaction. Approximately 3 inches of the empty tube served as a preheater which proved to be adequate (Figure 2). Curves 1 and 2 show the temperature distribution throughout the catalyst mass in a typical run at high air ratios. The maximum temperature shifted to various areas, depending on the air/toluene ratio and the time of contact. Curves 3 and 4 show the temperature distribution for a typical run at low air/toluene ratios. If the ratio is held constant and the time of contact decreased, the temperature will rise to abnormal heights as shown by the extended portion of curve 4. Below 500° C. the calorized tube had very little catalytic activity toward the complete combustion of toluene, even with a long time of contact. In run 2 (Table I) the total time for a molecule to pass through the tube was 30 seconds. Run 3 measured the activity of a Chromel screen which was to serve as a catalyst mass support in the reactor. However, it was discarded because the maximum temperature at the screen was 660° C. and 7.7 per cent of the toluene burned to carbon dioxide and water. An iron screen was investigated with equally unsatisfactory results. Runs 4 and 5 show that the activity of a perforated porcelain disk is negligible below 500° C.

The effect of varying the time of contact on the activity of a silica gel catalyst was determined. A long time of contact favored complete combustion. In run 6, assuming that all of the oxygen used in partial oxidation formed benzaldehyde, 25.2 per cent of the toluene passed was oxidized, 3.4 per cent
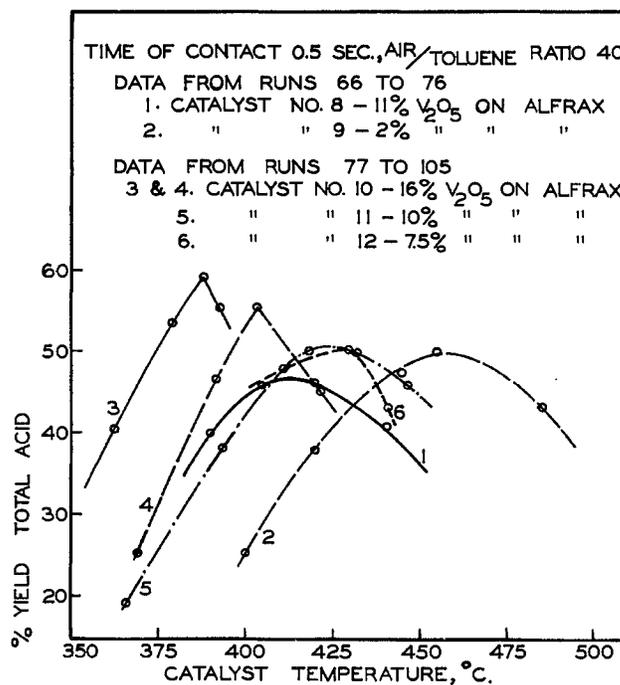
FIGURE 4.   EFFECT OF TEMPERATURE ON THE OXIDATION OF
TOLUENE

to carbon dioxide and water and 21.8 per cent to benzaldehyde. Calculated on the basis of the toluene reacted, 86.6 per cent was converted to benzaldehyde. The results indicate that the optimum time of contact for silica gel is approxi-

mately 1.5 seconds. When this material was used as a catalyst support, the optimum concentration of catalytic substance had to be determined for each catalyst.

Figure 3 indicates the effect of varying the air/toluene ratio for the three supports, silica gel, granular aluminum, and Alfrax. Alfrax showed the least activity toward complete combustion at the high ratios. The formation of a yellow oil was observed with the silica gel catalyst. The activity of silica gel toward complete combustion is very high, apparently approaching 100 per cent loss of toluene at ratios approaching the theoretical. Curves 2 and 3 show that both granular aluminum and Alfrax are relatively inert carriers with only slight catalytic activity toward complete combustion.
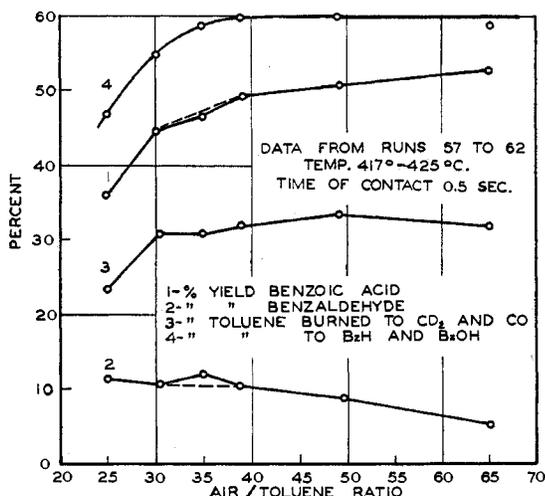
FIGURE 5. EFFECT OF VARYING THE AIR/TOLUENE RATIO WITH CATALYST 4 (7.7 PER CENT VANADIUM PENTOXIDE ON ALFRAX)

The results obtained with the following catalysts are not reported because the yields were unsatisfactory: cerium molybdate, and uranyl, iron, calcium, zinc, and silver vanadates. Iron vanadate supported on silica gel gave the best results in this group. At 400° C. with an air/toluene ratio of 4 and a high space velocity (short time of contact) a yield of approximately 8 per cent benzoic acid and 5 per cent benzaldehyde was obtained. Of the available oxygen, 91.4 per cent was consumed in complete combustion. A mixture of vanadium pentoxide and cesium vanadate on silica gel at 390° C., an air/toluene ratio of 11, and a very short time of contact produced approximately 10 per cent of both aldehyde and acid.

The catalytic activity of three different samples of vanadium pentoxide was investigated. With vanadium pentoxide obtained by decomposing vanadyl oxalate, supported on silica gel as the catalyst, the maximum conversion of toluene per pass to benzaldehyde and acid was 17.2 per cent. With commercial vanadium pentoxide supported on Alfrax as the catalyst, the maximum yield was 21 per cent per pass. A catalyst prepared by decomposing ammonium metavanadate on Alfrax at 300° C. (run 18) produced 22 per cent benzoic acid. The conditions of the run were not generally favorable to acid formation. An air/toluene ratio on the lean side of the explosive range increased the yield of acid to 51 per cent. On the basis of these results all further work was confined to vanadium pentoxide prepared by decomposing ammonium metavanadate. The effect produced by the three supports

using air/toluene ratios on the lean side of the explosive range was studied.

The results obtained with catalysts 3, 4, and 5 supported on Alfrax indicate that encouraging yields can be obtained with all concentrations of vanadium pentoxide. The lower concentrations appear to give higher yields, although they become active at higher temperatures. The differences in yield, however, may be due to a variation in activity between successively prepared catalysts. To investigate this possibility, catalyst 8 was prepared. The data are plotted in Figure 4, curve 1. After this series of runs sufficient vanadium pentoxide was removed by mechanical means to lower the concentration to 2 per cent (catalyst 9, curve 2, Figure 4). No attempt was made to secure an even distribution of the remaining catalytic material on the support. This catalyst attained its greatest activity at a temperature approximately 50° higher. These curves suggest the possibility that the aluminum oxide (Alfrax) may act as a promoter. The first period of peculiar activity exhibited by a freshly prepared catalyst (approximately 15 hours) was always eliminated before its behavior was studied.

The effect produced by using granular aluminum as the support was investigated by decomposing the ammonium metavanadate to the oxide on the aluminum at 300° C. The time necessary for decomposition on this support was much longer than that for Alfrax or silica gel. This may be attributed to the differences in structure. The aluminum is much more porous and holds the ammonium metavanadate more deeply embedded. There was evidence of a reaction between the aluminum and the ammonium metavanadate during the decomposition. This was indicated by the difference in color between the oxide resulting from the decomposition on Alfrax or silica gel and that on aluminum. In the former case the oxide was brick red when taken from the heating unit, and in the latter it was chocolate brown. Lower yields were obtained with this catalyst as shown by the following comparison:

12% Vanadium Pentoxide	Ratio	Contact Time, Sec.	Temp., ° C.	% Yield of Total Acid
On Alfrax	44.2	0.53	395–400	44.2
On porous aluminum	44.6	0.53	395–400	36.7

The yields obtained with a vanadium pentoxide on silica gel catalyst were lower than those obtained with aluminum as the support (run 31). Because of the hard glazed surface the maximum quantity of oxide which could be supported by this method of preparation was 3.8 per cent. These results indicate that Alfrax is the most satisfactory catalyst support. It is inactive, has a porous surface, and does not react with the ammonium metavanadate during decomposition. Silica gel has both mechanical and chemical defects. Besides possessing a high activity toward the complete combustion of toluene, it has a glazed, relatively nonporous surface. Granular aluminum (2) should be an excellent support because of its extremely porous nature and high heat conductivity. The latter property tends to give a more uniform temperature distribution. The low yields obtained may be attributed to some compound formation or impurity in the aluminum which poisoned the catalyst.

Figure 5 illustrates the effect of varying the air/toluene ratio with a catalyst containing 7.7 per cent vanadium pentoxide on Alfrax. The lean limit of the explosive range as calculated from volume percentages (15) is an air/toluene ratio of 25. The yield of partial oxidation products rises sharply as the ratio is increased beyond the explosive limit and appears to be constant above a ratio of 40. The ignition temperature of toluene is 500° C., and since the temperature of reaction is below this, ratios above 35 should be safe. From curves 1 and 2 it is evident that as the air/toluene ratio

TABLE I. EFFECT OF VARIOUS FACTORS ON THE VAPOR-PHASE CATALYTIC OXIDATION OF TOLUENE AT ATMOSPHERIC PRESSURE

	Catalyst	Vaporizer	Salt bath	Catalyst	Air/Toluene Ratio[a]	Time of Contact, Sec.[b]	Available O2 Consumed, %	% Consumed O2 Used in complete oxidation	% Consumed O2 Used in partial oxidation	% Toluene burned to CO2 and H2O	Benzaldehyde	Total acid	Maleic acid	Benzoic acid
1	None	98-95	.....	440-450	1.6	0.10	2.1	59.0	41.0	0.14	..	..	..	..
2	None	96-94	.....	450-455	1.7	2.05	9.1	76.8	23.2	0.97	..	..	..	..
3	Chromel gauze	95	.....	450	1.5	0.95	11.6	82.7	17.3	1.13	..	..	..	..
4	Perforated porcelain disk	96-95	.....	500-505	1.5	2.00	22.1	85.2	14.8	2.10	..	..	..	..
5		96-95	.....	450-455	4.4	0.25	3.1	64.6	35.4	0.80	..	..	..	..
6	Silica gel	96-95	.....	450-452	1.5	2.00	46.5	53.4	46.6	3.38	..	..	..	..
7		96-95	.....	500-507	1.5	2.00	96.5	75.2	24.8	9.50	..	..	..	..
8		96-95	.....	494-502	1.7	0.51	27.4	90.0	10.0	3.54	..	..	..	..
9	Alfrax	55-56	485-488	487-490	2.9	1.50	8.2	61.7	0.0	0.90	..	..	..	..
10		27-28	485-490	487-492	10.5	1.50	7.2	42.4	0.0	2.40	..	..	..	..
11	Granular aluminum	30-31	485-490	488-492	10.2	1.50	7.8	69.7	0.0	4.13	..	..	..	..
12		74-75	485-487	487-490	1.7	1.50	10.8	50.2	0.0	0.70	..	..	..	..
13	Catalyst 1, 12% V_xO_y on	75-76	330	390-400	10.5	0.22	28.7	75.1	24.9	16.80	8.8	8.4	..	..
14	silica gel	75-76	325-330	365-370	3.6	1.49	83.6	77.4	22.6	17.80	11.6	5.4	..	..
15		73-75	335-340	400-490	5.5	0.22	27.2	100.0	0.0	0.0	2.4	5.8	..	..
16	Catalyst 2, 12% V2O5 on	63-64	395-400	410-415	4.1	1.50	55.8	67.3	32.7	12.0	4.7	16.4	..	..
17	Alfrax	63-65	430-435	490	4.4	1.44	..	..	..	....	..	15.4	..	..
18	Catalyst 3, 3.5% V2O5 on	74-75	422-425	448-445	3.0	1.55	78.0	73.2	26.8	14.00	3.0	21.7	..	..
19	Alfrax	33-35	430-435	447-455	36.5	0.49	18.0	83.6	16.4	45.60	3.2	51.4	..	..
20	Catalyst 4, 7.7% V2O5 on	30-35	405-415	430-470	34.9	0.49	..	..	..	...	..	43.0	..	..
21	Alfrax	31-32	400-403	420-427	37.5	0.51	..	..	..	...	..	52.0	..	..
22		27	402-405	417-422	34.9	0.50	17.1	64.7	35.3	30.9	12.1	46.8	..	..
23		28	405-407	420-424	38.6	0.50	15.4	67.3	32.7	32.1	10.1	49.6	..	..
24		27	405-410	420-430	48.0	0.50	14.7	60.0	40.0	33.6	8.6	51.2	..	..
25		28	405-407	417-420	65.4	0.50	13.5	45.6	54.4	32.0	5.7	53.2	..	..
26	Catalyst 5, 12% V2O5 on	28-30	400-405	440-445	38.5	0.49	..	..	..	...	..	13.4	..	..
27	Alfrax	35-38	360-370	375-392	32.0	0.54	..	..	..	...	..	47.3	..	..
28		28	370-375	390-400	44.2	0.53	..	..	..	...	..	44.2	..	..
29	Catalyst 6, 12% V2O5 on	29	380-382	395-402	38.3	0.53	..	..	..	...	..	38.4	..	..
30	aluminum	27	343-345	350-352	45.9	0.55	..	..	..	...	..	26.9	..	..
31	Catalyst 7, 4.1% V2O5 on silica gel	29	376-387	402-415	46.5	0.50	..	..	..	...	..	30.5	..	..
32	Catalyst 8, 11.8% V2O5 on	28	395-396	415-420	52.2	0.51	..	..	..	...	..	34.8	..	..
33	Alfrax	26-27	385-390	404-403	40.0	0.51	..	..	..	...	..	46.0	..	..
34	Catalyst 9, 2.0% V2O5 on	27	408-410	420-422	49.4	0.50	..	..	..	...	..	48.7	..	..
35	Alfrax	27	388-392	397-402	40.6	0.50	..	..	..	...	..	25.5	..	..
36		26-27	435-440	454-458	38.7	0.50	..	..	..	...	..	50.0	..	..
37	Catalyst 10, 16% V2O5 on	27-28	335-340	342-348	37.5	0.50	..	..	..	...	..	27.0	..	..
38	Alfrax	28	368-372	384-387	39.4	0.50	..	..	..	...	..	59.0	..	..
39		26	375-374	394-395	45.4	0.50	..	..	..	...	..	47.7	..	..
40	Catalyst 11, 10.0% V2O5 on Alfrax	27	360-362	365-366	41.2	0.50	..	..	..	...	..	19.0	..	..
41		27	382-383	392	39.5	0.50	..	..	..	...	..	38.3	..	..
42		27	406-410	424-433	39.7	0.50	..	..	..	...	..	49.7	..	..
43	Catalyst 12. 7.5% V2O5 on	27	414-415	428-430	39.2	0.50	..	..	..	...	..	50.0	..	..
44	Alfrax	27	425-428	445-448	37.3	0.50	..	..	..	...	..	46.0	..	..
45	Catalyst 13, 6.2% V2O5 on	27	420-425	438-440	42.8	0.50	..	..	..	...	..	..	17.0	26.0
46	Alfrax	27	402-404	415-418	29.8	1.00	..	..	..	...	..	..	20.7	23.8
47		27	404-407	414-419	39.5	1.00	..	..	..	...	..	..	14.5	27.0
48		27	402-406	412-415	39.3	0.75	..	..	..	...	..	..	11.0	32.0
49		27	415-416	429-430	39.8	0.25	..	..	..	...	..	..	4.2	24.6
50		27	415	428-431	45.0	0.50	..	..	..	...	..	..	8.4	34.0

a Ratio of grams air per hour to grams toluene per hour.
b Ratio of volume of catalyst voids to volume of gas passing through catalyst per second at temperature of reaction.

increases, the yield of acid increases while that of benzaldehyde decreases. Curve 3 shows the quantity of toluene burned to carbon dioxide and carbon monoxide, as calculated from the gas analysis. The accuracy of these calculations is probably low as a result of the high air ratio. Furthermore, it was assumed that all carbon monoxide was produced by the incomplete combustion of toluene.

Green (4) reported that equimolecular quantities of oxygen and toluene vapor produced maximum yields of benzaldehyde. Gibbs (3) found that two and one-half times this concentration was desirable. Vanadium pentoxide was the catalyst in each case. Huitema and Brown (6) used tin vanadate as a catalyst and found that an even lower oxygen concentration was desirable. These results, together with what has been determined in this investigation, indicate that if the yield of partial oxidation products was plotted against the air/toluene ratio, a minimum would be exhibited within the explosive range. This is indicated by the slope of curve 4, Figure 5, at a ratio of 25. However, an investigation of the air/toluene ratios from 1 to 25 would be difficult because short times of contact cannot be employed at the low ratios due to

the large quantity of heat evolved. The use of a long time of contact was not feasible at high air/toluene ratios with the apparatus employed, as a result of the small quantity of toluene which passed through the reactor. The most satisfactory manner in which to secure a long time of contact is to increase the size of the reactor.

The results obtained from varying the catalyst temperature for catalysts 10, 11, and 12 are plotted in Figure 4. Curves 3 and 4 are the results from two series of experiments made with catalyst 10 and indicate the abnormal activity when freshly prepared. Curve 3 resulted after the catalyst had been in use for approximately 12 hours, and curve 4 after 24 hours. The conditions during this time were constant. A decrease in activity has occurred with continued use. The optimum temperature has shifted to a point 15° higher and the yield has decreased. Since the activity probably would not change greatly on further use, sufficient vanadium pentoxide was removed to produce catalyst 11. The results are shown by curve 5 and indicate a further decrease in activity. A catalyst suitable for commercial purposes must be capable of withstanding many hours of continuous operation with a

minimum loss of productive capacity. The only suitable method of definitely establishing the rate of depreciation of a catalyst is by continuous operation 24 hours a day for a long period. Curve 6 was obtained with a concentration of 7.5 per cent oxide. It is probable that catalyst 10 would have eventually reached the equilibrium shown by catalysts 11 and 12. These curves indicated that the activity may be independent of the vanadium pentoxide concentration above 7.5 per cent.

The partial oxidation products were not analyzed for maleic acid during the early part of this investigation. The results are reported as total acid and retained in this form because the curves illustrate the trend of the reaction with the change in variable involved. Notwithstanding the fact that maleic acid formation requires a rather complicated mechanism, a relatively large quantity is produced (Table I).
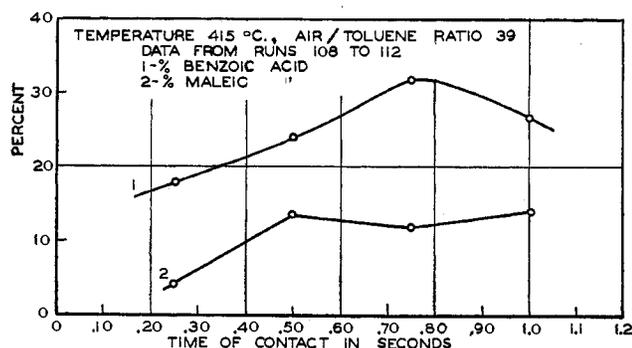
FIGURE 6. EFFECT OF TIME OF CONTACT ON CATALYST (6.2 PER CENT VANADIUM PENTOXIDE ON ALFRAX)

The formation of this acid was confirmed by melting point and solubility data. The technique of this analysis is important. The results reported are probably low because of mechanical loss and imperfect separation. The maleic acid values are higher than would be expected on the basis of earlier work (1, 3, 4, 6, 15). The anthraquinone was determined whenever it appeared desirable. The long yellow crystals which separated from the alcohol solution melted sharply at 285° C. The maximum yield was approximately 5 per cent. At low air ratios, as much as 40 per cent of the toluene oxidized per pass was converted to benzaldehyde. Also approximately 2 per cent of an easily reducible substance (probably quinone) was formed under certain conditions. The effect of varying the time of contact on the yield of benzoic and maleic acid is shown in Figure 6. The catalyst was 6.2 per cent vanadium pentoxide supported on Alfrax. A definite maximum appeared in the curve for benzoic acid.

With the proper choice of operating conditions and an efficient converter, fairly satisfactory yields of maleic and benzoic acid can be produced by this reaction. Benzaldehyde and anthraquinone may be recovered as by-products. Undoubtedly the per pass yields can be increased by further study of the operating conditions of the reaction, mode of preparation and concentration of the catalyst, other supports, tube size, relation of catalytic activity to particle size, and promoters.

Summary

1. The direct vapor-phase oxidation of toluene in the presence of solid catalysts to produce benzaldehyde and benzoic acid was investigated. The effect of temperature, time of contact, and air/toluene ratio was measured.

2. Calorized steel tubes showed very little activity toward the combustion of toluene at temperatures below 500° C. and time of contact less than 2 seconds. A maximum of 1.2 per cent of the toluene was burned to carbon dioxide and water.

3. Alfrax was a more satisfactory catalyst support than either granular aluminum or silica gel because less toluene was lost in complete combustion. Silica gel was the most active under all conditions. The Alfrax may act as a promoter.

4. The activity of three different samples of vanadium pentoxide showed considerable variation. The oxide prepared by decomposing ammonium metavanadate at temperatures below 300° C. was an excellent catalyst for the partial oxidation of toluene.

5. The most favorable air/toluene ratios for the formation of benzoic and maleic acids are on the lean side of the explosive range (> 25). As the ratio increases, the yield of acid increases and the yield of benzaldehyde decreases. If the ratio is held constant and the time of contact decreased, the catalyst temperature increases rapidly.

6. The maximum yields of partial oxidation products were: total acid 59 per cent, maleic acid 21, benzoic acid 34, benzaldehyde 12, and anthraquinone 5, on the basis of the toluene oxidized per pass. The most important variables in this reaction are temperature and method of catalyst preparation.

7. A yield of 21.5 per cent maleic acid and 22.0 per cent benzoic acid was obtained at 416–419° C., air/toluene ratio 31, and time of contact 1 second. The catalyst was 6.2 per cent vanadium pentoxide on Alfrax.

8. The low air ratio and short time of contact favorable to aldehyde formation are not easily controlled because the quantity of toluene oxidized per unit volume of catalyst is too large for the heat removal capacity of the converters.

9. The results indicate that good yields can be obtained with all concentrations of vanadium pentoxide above 6.2 per cent. The lower concentrations give higher yields but become active at higher temperatures.

Acknowledgment

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