Catalytic Partial Oxidation of Alcohols in the Vapor Phase.   IV

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THE importance of heat transfer in vapor-phase catalytic oxidation has been recognized for some time. A number of patents have been issued concerning vapor-phase oxidation, in which the basic features pertain to an improvement in heat transfer within the process. The significance of heat transfer in this connection has also been pointed out by Downs (2), Huff (5), and Parsons (6). More recently Faith and Keyes (3) have shown that in the vapor-phase catalytic oxidation of alcohols the metallic form of a specific catalyst gives higher conversion to intermediate oxidation products (i. e., aldehyde and acid) than a catalyst of the same metal deposited on asbestos.

This effect of heat transfer within the catalyst itself is so marked that it was thought advisable to study also the effect of heat transfer through the walls of the catalyst chamber. In the authors' previous studies the catalyst was always placed in a Pyrex tube. Whether the heat from the catalyst is dissipated by radiation or conduction or both, it is obvious that the glass tube is inefficient as a heat-transfer medium.

The catalytic oxidation of ethyl alcohol in the vapor phase has been studied. Four types of catalyst chambers, designed to improve heat transfer and temperature control, have been described.

The following variables have been studied: (1) continuous vs. intermittent heating, (2) copper tube vs. Pyrex tube as catalyst chamber, (3) thin-walled vs. heavy-walled catalyst chambers, and (4) alcohol-air ratio.

The effects of catalyst temperature and time of contact as independent variables are shown. The yields of intermediate oxidation products under conditions favorable for reasonably high conversions are higher than any heretofore published.
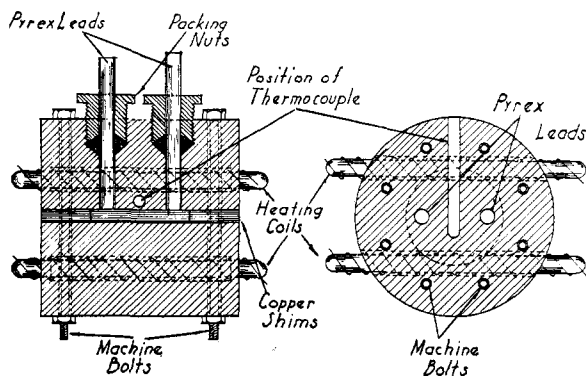
of catalyst chambers, four of which will be described later. Two distinct methods of heating the chambers were employed. The first three types of catalyst chambers were heated continuously during the time the run was being made. The fourth type was heated intermittently, but nevertheless the temperature was controlled very closely.

The oxidation of ethyl alcohol was chosen as the reaction to be studied because of its flexibility and ease of control. Pure anhydrous ethyl alcohol was used in this investigation. Copper was chosen as the catalyst, since with it a catalytic mass of high uniform activity could be easily reproduced. The catalyst was in every case activated by alternate oxidation and reduction at successively lower temperatures.

The analytical methods also have been described previously by Faith and Keyes (3).

SLIT-TYPE CATALYST CHAMBER. The type of catalyst chamber that was first substituted for the Pyrex tube is shown diagrammatically in Figure 1.

It consists of two cylindrical copper blocks, 10.2 cm. (4 inches) in diameter and 3.8 cm. (1.5 inches) in height. One of these blocks is fitted with packing nuts arranged as shown, so that airtight connections may be made with the Pyrex glass leads. Graphitized asbestos wicking is used as the packing material. The catalyst space itself consists of a thin section or slit between the two blocks, which are separated by thin copper shims. The width of the slit may be varied by changing the number of spacers. The center opening is 3.8 cm. (1.5 inches) in diameter, and the distance between the centers of the holes through which the gas enters and leaves the block is 2.5 cm. (1 inch). The two halves of the chamber are held tightly together by eight machine bolts spaced symmetrically around the block. Through the sections of the blocks and parallel with the diameter are four holes about 1.27 cm. (0.5 inch) in diameter. Heating coils of chromel wire wrapped on a Pyrex glass core are embedded in alundum cement in these openings. An electric current through these coils serves to maintain the catalyst block at the desired temperature. Auxiliary heating is obtained by use of a hotplate heater. A hole in one of the blocks very near the active catalyst surface serves to receive the thermocouple which measures the temperature of the catalyst.

The walls of the slit opening, which themselves serve as the catalyst, are activated in the same manner as a copper-turnings catalyst. Three different slit widths were used—viz., 0.025, 0.05, and 0.075 cm. (0.01, 0.02, and 0.03 inch).

FIGURE 1. SLIT-TYPE CATALYST CHAMBER

It was therefore decided to replace the glass tube in some manner with a material which is a better radiator and conductor than glass, and through which better temperature control can be maintained.

This improvement should eliminate in a large measure the undesirable effects due to accumulation of excess heat— e. g., detrimental side reactions and complete oxidation.

EXPERIMENTAL PROCEDURE AND APPARATUS

A detailed description of the apparatus used was given in a previous paper (3), with the exception of the different types

It is easily seen that this type of catalyst chamber permits only a short time of contact and very good temperature control, since the catalyst is actually a part of the block.

A few of the results characteristic of this type of catalyst chamber are shown in Tables I and II. Results using the 0.025-cm. (0.01-inch) slit are not shown, since after one or two runs the slit invariably became clogged with copper oxide and could not be used further.

TABLE I. RESULTS USING SLIT-TYPE CATALYST CHAMBER AND COPPER CATALYST

(Thermostat, 45° C.; flow, 0.61 liter per minute; slit, 0.05 mm.)

			CONVERSIONS			
TEMP.	Aldehyde	Acid	Total intermediate products	CO₂	Total	YIELD
° C.	%	%	%	%	%	%
385	20.2	1.0	21.2	6.1	27.3	77.6
400	38.5	1.5	40.0	7.0	47.0	85.1
455	49.5	4.7	54.2	14.7	68.9	80.0
500	53.2	5.1	58.3	14.8	73.1	..
555	49.6	1.6	51.2	10.8	62.0	..
590	47.6	2.5	50.1	11.0	61.0	..

TABLE II. RESULTS USING SLIT-TYPE CATALYST CHAMBER AND COPPER CATALYST

(Thermostat, 45° C.; catalyst temperature, 510° C.; slit, 0.075 mm.)

			CONVERSIONS			
FLOW	Aldehyde	Acid	Total intermediate products	CO₂	Total	YIELD
Liter/min.	%	%	%	%	%	%
0.38	57.8	4.0	61.8	29.1	90.9	68.0
0.54	52.2	4.1	56.3	15.6	71.9	78.3
0.59	48.2	3.0	51.2	13.9	65.1	78.6
0.74	44.3	3.2	47.5	13.4	60.9	78.0

For the sake of comparison, the results obtained using a Pyrex tube as a catalyst chamber are shown in Table III.

TABLE III. RESULTS USING PYREX-TUBE CATALYST CHAMBER AND COPPER-TURNINGS CATALYST

(Thermostat, 45° C.; catalyst length, 45 mm.; catalyst diameter, 13 mm.)

				CONVERSIONS			
FLOW	TEMP.	Aldehyde	Acid	Total intermediate products	CO₂	Total	YIELD
Liter/min.	° C.	%	%	%	%	%	%
0.51	462	71.0	3.1	74.1	12.0	86.1	86.1
0.52	465	72.0	3.5	75.5	12.0	87.5	86.3
0.55	470	73.0	3.3	76.3	11.6	87.9	86.7
0.60	488	76.0	4.6	80.6	12.4	93.0	86.6
0.62	512	78.0	2.8	80.8	14.1	94.9	85.1
0.64	517	77.0	2.6	79.6	13.5	93.1	85.5
0.65	520	76.5	2.2	78.7	10.9	89.6	87.8
0.66	522	76.0	2.0	78.0	11.1	89.1	87.5
0.74	542	74.0	1.3	75.3	11.4	86.7	86.8

COPPER BLOCK–GLASS TUBE CATALYST CHAMBER. A slightly modified form of the above copper-block catalyst chamber is shown in Figure 2.

It is a cylindrical copper block 5.1 cm. (2 inches) in diameter and 10.2 cm. (4 inches) in length. Longitudinally through its center is a 6.0-mm. (0.25-inch) hole, fitted at each end with packing nuts for making connections with glass tubing. In operation this tube is tightly packed with copper turnings which act as the catalyst. This block also carries heating coils and a hole for the thermocouple similar to those described above.

The results obtained using this catalyst chamber are quite similar to those obtained with the slit chamber.
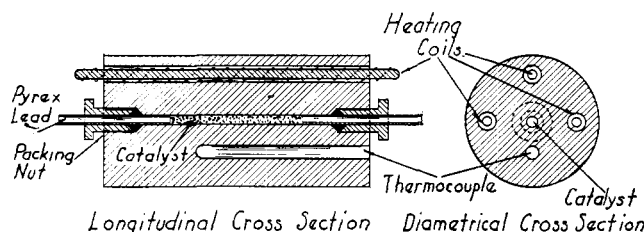

Longitudinal Cross Section   Diametrical Cross Section

FIGURE 2. COPPER BLOCK–GLASS TUBE CATALYST CHAMBER

COPPER BLOCK–COPPER TUBE CATALYST CHAMBER. The third type of catalyst chamber used is shown in Figure 3. It is much like the last chamber described with two exceptions. First, copper leads are used instead of Pyrex; second, the catalyst itself, which is made of copper turnings, is identical in size with that used in the Pyrex catalyst tube.

The results obtained using this style of catalyst chamber are shown graphically in Figures 4 and 5.

COPPER-GLASS SEAL CATALYST CHAMBER. The fourth type of catalyst chamber used is much simpler in design than the other three described. In making this tube, advantage is taken of the direct copper-to-glass seal commonly known as the Housekeeper seal (4).

A very thin copper tube about 7.6 cm. in length and approximately 13 mm. inside diameter is sealed on both ends to Pyrex tubes of convenient size. Copper turnings are placed inside the copper tube and activated in the same manner as described above. In the assembled apparatus a removable furnace is placed around the copper section of the tube.

A thermocouple is embedded in the center of the catalyst mass and protected by a very thin-walled Pyrex tube in the same manner as described previously (3).
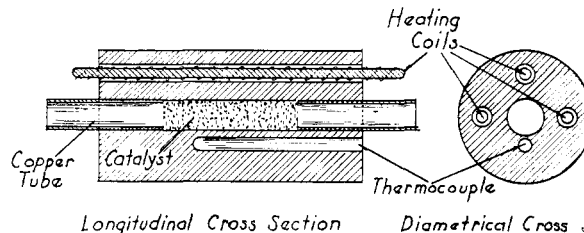

Longitudinal Cross Section   Diametrical Cross Section

FIGURE 3. COPPER BLOCK–COPPER TUBE CATALYST CHAMBER

The results obtained using this tube are shown in Table IV. A few results using a Pyrex tube are added for comparison.

In all of the tables both conversions and yields are tabulated. Conversion data are calculated on the basis of the total amount of alcohol passed over the catalyst in one run. The yields given are based on the actual amount of alcohol that reacts during a single pass over the catalyst.

TABLE IV. COMPARISON OF RESULTS USING COPPER-GLASS SEAL CATALYST CHAMBER WITH THOSE USING PYREX-TUBE CATALYST CHAMBER [a]

(Catalyst length, 45 mm.; catalyst diameter, 13 mm.)

THERMOSTAT TEMP.	ALCOHOL-AIR RATIO	FLOW	TEMP. CATALYST	Aldehyde	Acid	Total intermediate products	CO₂	Total	YIELD
° C.	Gram[b]	Liter/min.	° C.	%	%	%	%	%	%
			COPPER-GLASS SEAL CATALYST CHAMBER						
45.0	0.37	0.57	450	48.3	6.8	55.1	22.9	78.0	70.6
45.0	0.38	0.61	480	49.6	6.9	56.5	24.6	81.1	69.9
52.0	0.47	0.65	430	62.6	7.1	69.7	9.5	79.2	88.0
52.0	0.46	0.68	450	56.5	6.1	62.6	10.9	73.5	85.3
53.0	0.59	0.54	435	54.9	7.4	62.3	13.0	75.3	82.7
53.0	0.59	0.57	435	57.5	7.4	64.9	10.7	75.6	85.8
54.0	0.62	0.57	415	55.4	6.8	62.2	7.7	69.9	88.9
54.0	0.62	0.62	430	53.9	6.0	59.9	8.0	67.9	88.2
55.0	0.63	0.51	425	59.0	5.4	64.4	7.0	71.4	90.2
55.0	0.57	0.61	435	62.1	5.2	67.3	9.8	77.1	87.5
57.0	0.77	0.51	415	56.8	4.1	60.9	3.5	64.4	94.5
57.0	0.74	0.54	425	57.8	5.6	63.4	4.2	67.6	93.8
59.0	0.84	0.51	410	51.0	4.2	55.2	2.4	57.6	95.8
59.0	0.83	0.51	420	54.8	5.1	59.9	4.4	64.3	93.1
61.0	0.94	0.48	410	54.7	4.4	59.1	1.6	60.7	97.3
61.0	0.93	0.51	420	51.0	3.5	54.5	2.4	56.9	96.1
			PYREX-TUBE CATALYST CHAMBER						
45.0	0.38	0.51	462	71.0	3.1	74.1	12.0	86.1	86.1
45.0	0.38	0.52	465	72.0	3.5	75.5	12.0	87.5	86.3
54.0	0.66	0.57	415	56.0	2.4	58.4	6.0	64.4	90.6
57.0	0.77	0.51	415	53.9	1.8	55.7	4.1	59.8	93.1
61.0	0.97	0.51	410	52.7	1.3	54.0	2.1	56.1	96.3
61.0	0.94	0.61	420	45.6	1.5	47.1	2.2	49.3	95.6

[a] Copper-turnings catalyst used in both cases.
[b] Grams ethyl alcohol per liter of air.

DISCUSSION OF RESULTS

The course of the oxidation reaction is appreciably influenced by each of the first three catalyst chambers described. The results obtained with these catalyst chambers, when compared with those obtained with the Pyrex catalyst tube, show a slight increase in conversion to carbon dioxide, a greater increase in conversion to acetic acid, and a decided decrease in conversion to aldehyde.

In each of these cases, heat was added continuously to the system. Day (1), in his studies on the catalytic oxidation of ethyl alcohol in the vapor phase, has heated the catalyst in
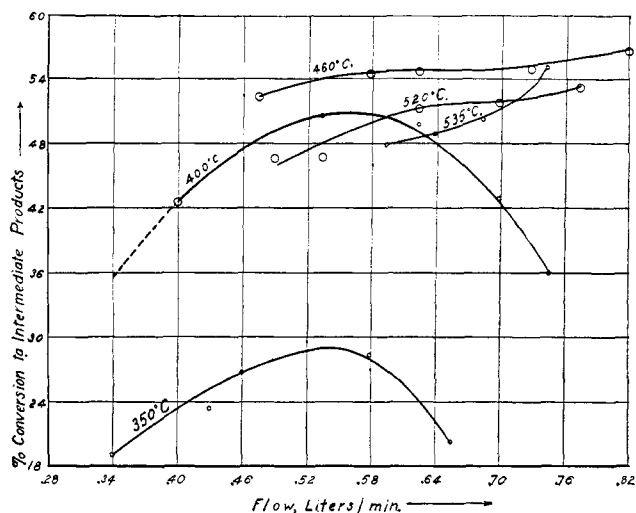
FIGURE 4. CONVERSION TO INTERMEDIATE PRODUCTS IN OXIDATION OF ETHYL ALCOHOL, USING COPPER AS CATALYST

like manner. Using a silver catalyst in different types of catalyst chambers, he has observed effects similar to those described above.[1]

Considering the actual amount of catalyst used, the conversions with the slit-type catalyst chamber are very good. At the same time, the conversion to carbon dioxide is quite high. This can be attributed either to an inactive catalyst or to excessive temperature or both. It is quite probable that the temperature of the catalytic surface was higher than that recorded by the thermocouple embedded in the copper block.

The poor conversions in the copper block–copper tube catalyst chamber are undoubtedly caused by a heating zone which is too long. Since copper is a good heat conductor, the entrance and exit copper tubes become very hot. Thus, the incoming gases are preheated to a temperature detrimental to a high conversion (1), and the products in the exit gases are subjected to further reaction.

However, the results obtained using this catalyst chamber show very clearly the effect of temperature and time of contact on the vapor-phase oxidation of ethyl alcohol. These results are given because the effect of temperature and of time of contact, each independent of other variables, has never been shown in any published article. By examining the graphs in Figures 4 and 5, it may be seen that:

1. Maximum conversion depends upon temperature.
2. At temperatures below the maximum conversion, the lower flows give the highest conversions to intermediate products, because the alcohol remains in contact with the catalyst for a longer time.
3. At temperatures above the maximum conversion, higher flows give slightly better conversions to intermediate products owing to prevention of formation of carbon dioxide from aldehyde.

The fourth catalyst chamber—the copper-glass seal chamber—was designed to avoid the defects inherent in the previously mentioned chambers. Thus, the catalyst was increased to the same size as that used in the Pyrex tube experiments and placed in the copper tube to give better radiation and conduction than could be obtained with the glass tube. The entrance and exit tubes to the main catalyst chamber were made of glass to prevent a large longitudinal flow of heat along these tubes, thus preventing excessive

[1] Private communication.

preheating of the incoming gases and thermal decomposition of the products in the exit gas. In short, in this catalyst chamber the heat is confined largely to that portion of the catalyst chamber directly in contact with the catalyst. The protected thermocouple junction was inserted directly into the catalyst mass to give a more nearly accurate estimation of the catalyst temperature. Furthermore, this catalyst chamber was heated intermittently instead of continuously, because the results obtained by Day,[1] together with the results shown in Tables I and II, indicate that continuous heating is detrimental to high yields and conversions.

In the experiments using this catalyst tube, the alcohol-air ratio was varied by changing the temperature of the thermostat. At the lower alcohol-air ratios the plain Pyrex catalyst chamber gives the higher conversions and yields of intermediate products, but the copper-glass seal tube gives much better conversions and yields of acetic acid. However, at the higher alcohol-air ratios which are conducive to high total yields, the copper-glass seal tube not only gives higher acid conversions and yields, but also higher total conversions and yields to intermediate products.

The oxidation of ethyl alcohol to acetic acid is a reaction which requires very close temperature control, and without such control high yields of acid cannot be obtained. Examination of Table IV shows that the increase in conversion
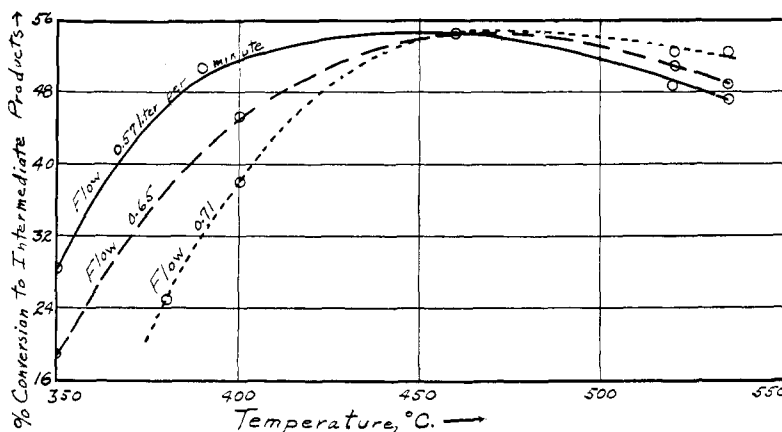

FIGURE 5. CONVERSION TO INTERMEDIATE PRODUCTS IN OXIDATION OF ETHYL ALCOHOL

to acid accounts almost entirely for the higher total conversions and yields obtained with the copper-glass seal tube. This shows clearly that strict temperature control is effected in this case. This close control, in turn, is due to the high heat transfer of the catalyst chamber. Also, it is obvious that this increase in heat transfer, which contributes to the increase in conversion to acid, also favors high yields and total conversion to all intermediate products.

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