

Acknowledgment

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Literature Cited

- (1) Edwards, J. D., Frary, F. C., and Jeffries, Z., "The Aluminum Industry," 1st ed., Vol. 1, p. 216, McGraw-Hill, 1930.
- (2) Waggaman, S. J., and Cullen, S. J. A., U. S. Dept. Agr., *Bull.* **415** (1916).

Catalytic Partial Oxidation of Alcohols in the Vapor Phase—III^{1,2}

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VAPOR-phase partial oxidation offers great possibilities in solving the problems of modern chemical industry. This has been shown by the excellent work of Jaeger, Downs, and others on the partial oxidation of benzene, naphthalene, and anthracene.

However, before this work can be extended to the oxidation of other organic compounds, much study must be made on the fundamental nature of oxidation catalysis. The vapor-phase partial oxidation of alcohols offers a convenient system for such a study, since all variables may be easily controlled.

The greatest criticism of recent work on partial oxidation of alcohols is that each investigator has used an entirely different apparatus in his work, and that work done when using one apparatus is not duplicable when using another.

Therefore, it was decided to devise an apparatus of simple construction, which might be easily reproduced and, by means of which, investigations on vapor-phase partial oxidation of alcohols might be accurately and easily duplicated.

In an article on ammonia oxidation, Parsons (8) has pointed out that platinum is much preferred to nonmetallic catalysts since it simplifies the local overheating problem.

It was, therefore, thought probable that the form of a particular catalyst which permits the greatest amount of radiation will yield the best conversions of intermediate products (i. e., aldehyde and acid) in the oxidation of alcohols. In other words, that form of a catalyst which has the highest coefficient of heat transfer could be maintained at a more uniform temperature than any form of the same catalyst

The catalytic partial oxidation of ethyl alcohol and methanol has been carried out. Different forms of silver, copper, and nickel catalysts have been used. It has been found that the form of catalyst having the highest coefficient of heat transfer gives the highest conversion of intermediate products. A laboratory apparatus for obtaining duplicable results has been constructed and described.

which has a lower heat-transfer coefficient.

This was thought to be true because a catalytic reaction will take place largely at the most active spots, or regions, in the catalyst. If the reaction is exothermic, this will cause

a localized accumulation of heat and therefore an increase in temperature at these active spots. Unless this heat can be conducted away from these localized high-temperature regions, the reaction (in this case an oxidation) will be carried to completion instead of stopping at an intermediate point. If the catalyst itself has a high heat-transfer coefficient, it should conduct the heat away from these regions and stop the reaction at the desired stage by keeping the entire catalyst at a lower and more uniform temperature.

In order to show this clearly, it was decided to use several catalysts (each in two different forms), one of which had a high and one a low coefficient of heat transfer. To test this theory more thoroughly, catalysts of markedly different activity were chosen for this reaction, i. e., silver, copper, and nickel. The metallic form of each of these was chosen for that form having good heat transfer, while the oxide of each, deposited on asbestos fiber, was chosen for the form having poor heat transfer.

Apparatus and Procedure

The apparatus used is shown in Figure 1.

Air was passed through a flowmeter, where rate of flow was measured, thence through a drying tower containing CaCl_2 , to the preheater. The preheater was simply a copper coil immersed in the thermostat. From the preheater, air could be led into the furnace by any one of three means. At first, stopcock *a* was so turned that air passed through carburetor *A*, and thence through stopcock *d*, to tube leading to furnace. Previously, alcohol had been let into carburetor *A* by means of the dropping funnel shown.

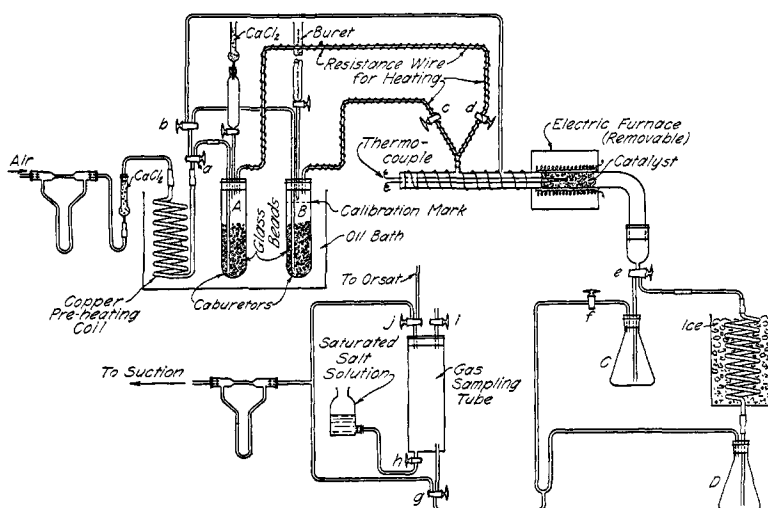


Figure 1 - Apparatus for Vapor-Phase Partial Oxidation of Alcohols

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² Part I, "Studies in Liquid Partial Oxidation—I," *IND. ENG. CHEM.*, **21**, 1227 (1929); Part II, "Studies in Liquid Partial Oxidation—II," *Ibid.*, **23**, 561 (1931).

³ Submitted by W. Lawrence Faith in partial fulfillment of the requirements for the degree of doctor of philosophy in chemistry in the Graduate School of the University of Illinois.

After the reaction in the catalyst chamber had reached equilibrium, stopcocks *a* and *b* were so turned that air entered carburetor *B*. Carburetor *B* had been previously filled with alcohol up to the calibration mark shown on the carburetor. It was through the alcohol in this carburetor that air was passed during the run. During the run, alcohol was allowed to run from the buret into the carburetor from time to time, and when the run was completed, the carburetor was filled to the calibration mark and a buret reading was made. This measured the amount of alcohol vaporized during the run. A thermometer hanging along the side of the buret showed the temperature of the alcohol and thus made it possible to calculate the weight of alcohol used up. This usually varied from 10 to 20 grams.

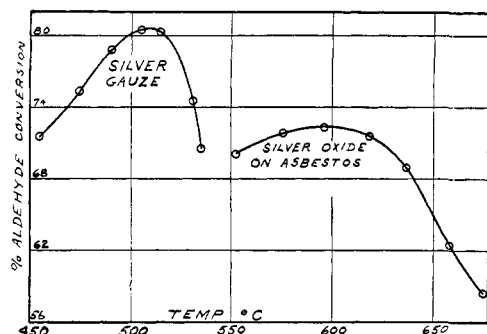


Figure 2—Conversion of Aldehyde from Oxidation of Ethyl Alcohol, Using Silver as Catalyst

While the run was being made, stopcock *d* was closed to prevent vaporization of alcohol from carburetor *A*, since this would allow more alcohol to pass through the furnace than would be indicated by the buret reading. Likewise, during the time when the reaction was reaching equilibrium by vaporizing the alcohol in carburetor *A*, stopcock *c* was closed to prevent vaporization of alcohol from carburetor *B*.

Another means of introducing air into the catalyst chamber was that of turning stopcocks *a* and *b* so as to shunt the air around the carburetors. This was used in passing air or hydrogen into the catalyst chamber to activate the catalyst.

Around the tubes, through which air and alcohol passed on the way to the catalyst chamber, resistance wire was wrapped and heated to prevent condensation of alcohol in these tubes.

The thermostat heater was regulated by means of a mercury regulator and relay; the oil was circulated by a motor-driven stirrer.

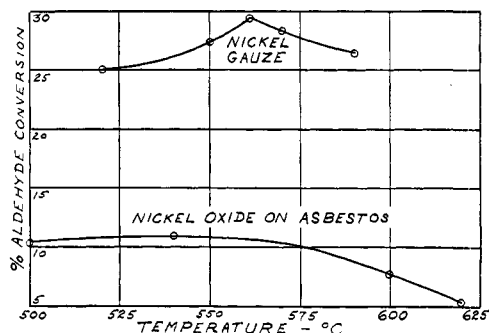


Figure 4—Conversion of Aldehyde from Oxidation of Ethyl Alcohol, Using Nickel as Catalyst

During the preliminary period, while equilibrium was being set up, the reaction products which came from the catalyst chamber were run into collection flask *C* and out through stopcock *f*. After reaching equilibrium, and while alcohol was being vaporized from carburetor *B*, the reaction products

were run through an ice condenser into collection flask *D*. Stopcock *f* was closed to prevent vaporization of liquid from collection flask *C* and subsequent incorrect analysis.

At *D*, a portion of the liquid products and practically all of the unchanged alcohol were collected. The gaseous products and some of the aldehyde formed passed through a flowmeter to the atmosphere.

A gas sampling tube was placed in the line and the effluent gases were analyzed in a modified Orsat for aldehyde, carbon dioxide, oxygen, and carbon monoxide. The operation of the gas sampling tube shown in the figure is evident. The carburetors *A* and *B* were long and narrow and partially filled with glass beads to afford good contact between the air and alcohol.

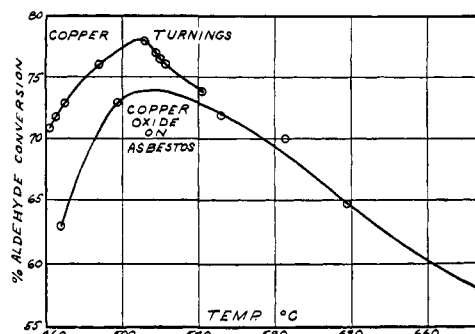


Figure 3—Conversion of Aldehyde from Oxidation of Ethyl Alcohol, Using Copper as Catalyst

The catalyst tube was made of Pyrex glass, because a metal tube would probably lend either promoting or inhibiting action to the catalyst. The catalyst was 45 mm. long and 12 mm. in diameter. A thermocouple protected by a very thin-walled Pyrex tube was imbedded in the metallic catalyst. In this way good contact with the metallic catalyst was afforded, so that its temperature was accurately recorded. However, in the cases where asbestos fiber was used as a support for the catalyst, it was impossible to record the exact temperature of the catalyst. In this case, the junction of the thermocouple was placed in the glowing part of the catalyst. It was found that the highest temperature was recorded by so placing the thermocouple junction. In the catalysts supported on asbestos, a temperature gradient of 250° C. existed in 40 mm. of the catalyst. However, in the case where a metallic catalyst was used, the temperature was uniform throughout. The catalyst was always heated to 350° C. before a run was started, after which time it generally maintained itself at a definite temperature.

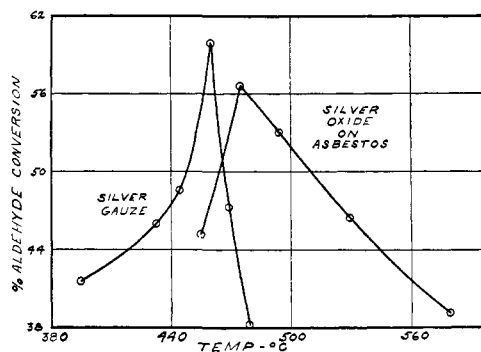


Figure 5—Conversion of Aldehyde from Oxidation of Methanol, Using Silver as Catalyst

Anhydrous alcohols were used throughout the experiment to prevent water from concentrating in the carburetors and lowering the vapor pressure of the alcohol.

The advantages of this apparatus are obvious. First, the

entire run is made under the same conditions; and secondly, an elaborate scrubbing system is eliminated. Accurate and easily duplicable results are quickly obtained.

Preparation and Activation of Catalysts

The catalysts used were copper, silver, and nickel. Each one was used both in the metallic form and as an oxide deposited on asbestos fiber.

COPPER CATALYST—The metallic catalyst consisted of copper turnings packed tightly in the catalyst tube. This catalyst was activated by alternately oxidizing and reducing it at successive lower temperatures from 600° to 250° C. In the other case, copper oxide was ground very fine in a mortar, the oxide suspended in water, intimately mixed with asbestos fiber, and dried. The catalyst was then activated in the same manner as the metallic catalyst.

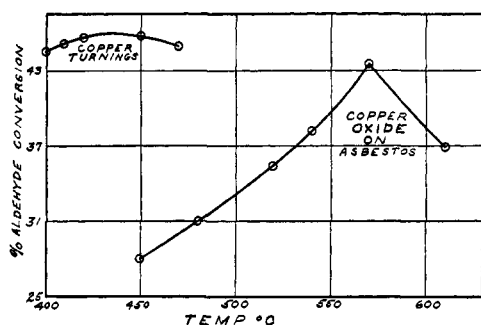


Figure 6—Conversion of Aldehyde from Oxidation of Methanol, Using Copper as Catalyst

SILVER CATALYST—Silver gauze was tightly wound around the thermocouple protector tube and forced into the catalyst tube.

Since silver is not easily oxidized by oxygen, it was activated by alternate oxidation by ozone and reduction by hydrogen. The first ozonization was carried out at 220° C. Subsequent ozonization could be carried out at room temperature. The oxygen, before entering the ozonizer, was bubbled through water since dry ozone will not oxidize silver (6). The silver catalyst made by deposition of silver oxide on asbestos fiber was activated in the same manner.

NICKEL CATALYST—Nickel gauze treated in the same manner as silver gauze was placed in the catalyst tube. It was activated in the same manner as copper catalyst.

Nickel oxide deposited on asbestos was treated likewise.

Oxidation of Ethyl Alcohol

Pure anhydrous ethyl alcohol, free from aldehydes, was used. The kind and amounts of catalysts used have been enumerated in the preceding section.

The thermostat temperature was 45° C. In preliminary work, this was shown to be the optimum vaporization temperature for acetaldehyde conversion.

DETERMINATION OF ACETALDEHYDE—The aldehyde in the condensate was determined by the neutral sodium sulfite method (4).

DETERMINATION OF ACETIC ACID—The acid in the condensate was titrated with *N* sodium hydroxide solution. The acid was identified by the method of DuClaux, as described by Kamm (3).

DETERMINATION OF UNCHANGED ETHYL ALCOHOL—The unchanged ethyl alcohol was determined by the ammoniacal silver nitrate method described by Lowdermilk and Day (5).

ORSAT ANALYSIS—The gas sample was delivered from the sampling tube to the Orsat and then passed through 30 per cent sodium acid sulfite solution to determine aldehyde.

Carbon dioxide was determined by passing the residual gas through 30 per cent potassium hydroxide solution.

Oxygen was taken out by alkaline pyrogallol solution, and carbon monoxide was then determined by absorption in ammoniacal cuprous chloride solution.

Oxidation of Methanol

Pure anhydrous methanol, free from acetone, was used. The same catalysts and amounts of catalysts were used as with ethyl alcohol. The temperature of the oil-bath thermostat was 36° C.

No attempt was made to find the optimum temperature of the thermostat for best formaldehyde conversion; 36° C. was chosen because the vapor pressure of methanol at this temperature is approximately the same as ethyl alcohol at 45° C., the bath temperature used in that experiment.

DETERMINATION OF FORMALDEHYDE—The same method as for the determination of acetaldehyde was used.

DETERMINATION OF UNCHANGED METHANOL—The unchanged methanol was determined by the method of Blank and Finkenbeiner (2). This method was chosen because the presence of methylal will not interfere and invalidate the analysis. This point has recently been discussed by Adkins and Petersen (1).

DETERMINATION OF FORMIC ACID—The acid formed in this oxidation was titrated with *N* sodium hydroxide. Only a trace was found in the reaction products of each run, rendering identification impossible.

Discussion of Results

The apparatus developed in this investigation operated very satisfactorily. The fact that the reaction had reached equilibrium before a run was started undoubtedly contributed to the high conversions obtained. (See Tables I and II.) The value of the apparatus is further enhanced by the fact that operating conditions and results could be duplicated at any time. Cooling the reaction products quickly in an ice condenser after leaving the catalyst also prevented complete combustion and pyrolysis from taking place.

Table I—Results of Oxidation of Ethyl Alcohol
Thermostat 45° C., length of catalyst 45 mm.

CATALYST	FLOW Liter/min.	TEMP. ° C.	CONVERSIONS		
			Aldehyde %	CO ₂ %	Acid %
Silver gauze	0.43	455	71.6	14.7	2.5
	0.45	475	75.4	13.5	2.1
	0.48	490	78.9	12.9	2.1
	0.54	505	80.5	12.8	2.7
	0.57	515	80.6	13.3	3.2
	0.61	530	74.7	12.7	2.1
Silver oxide on asbestos	0.64	535	71.6	13.2	2.2
	0.25	552	70.2	13.6	2.3
	0.30	578	71.9	13.8	2.1
	0.37	595	72.3	14.5	2.9
	0.42	620	71.8	14.9	2.9
	0.48	640	69.0	14.8	2.8
Copper turnings	0.54	658	62.5	14.3	3.3
	0.58	675	58.5	14.3	2.6
	0.51	462	71.0	12.0	3.1
	0.52	465	72.0	12.0	3.5
	0.55	470	73.0	11.6	3.3
	0.60	488	76.0	12.4	4.6
Copper oxide on asbestos	0.62	512	78.0	14.1	2.8
	0.64	517	77.0	13.5	2.6
	0.65	520	76.5	10.9	2.2
	0.66	522	76.0	11.1	2.0
	0.74	542	74.0	11.4	1.3
	0.31	468	63.0	14.3	2.8
Nickel gauze	0.37	498	73.0	12.6	2.6
	0.52	552	72.0	12.6	2.6
	0.57	586	71.2	15.3	2.7
	0.65	618	65.0	15.2	2.7
	0.82	687	58.0	14.0	2.8
	0.34	520	25.1	16.7	0.4
Nickel oxide on asbestos	0.43	550	27.5	21.7	0.6
	0.45	560	29.6	18.9	0.5
	0.48	570	28.4	18.2	0.6
	0.54	590	26.5	17.5	0.7
	0.28	500	10.5	14.6	Trace
	0.31	540	10.9	14.0	Trace
	0.37	600	7.7	13.6	Trace
	0.40	620	5.5	16.0	Trace

The maximum error found in runs with the same catalyst was ± 1 per cent. Runs using a fresh catalyst each time were subject to an error of ± 2 per cent, since it is extremely difficult to duplicate the catalyst exactly.

The analysis for aldehyde in the vapor phase by means of a modified Orsat eliminated the elaborate scrubbing system which would have been necessary otherwise. This analysis proved very satisfactory, being subject only to the usual error of Orsat gas analysis.

The results show that in all cases the form of catalyst with the highest heat-transfer coefficient gave the highest conversions of intermediate products. In the oxidation of ethyl alcohol, higher conversions of acetaldehyde have been obtained than in any previously reported.

Using copper turnings, Lowdermilk and Day (5) obtained a conversion of 70.5 per cent of the alcohol to acetaldehyde. The best reported conversion using silver gauze is by Moureu and Mignonac (7). They obtained a conversion of 73.0 per cent. The conversions which the present authors obtained were 78.0 and 80.6 per cent, respectively. Using two silver-gauze catalysts in series, Moureu and Mignonac (7) obtained an 84.0 per cent conversion to acetaldehyde. However, this is not comparable to the present work.

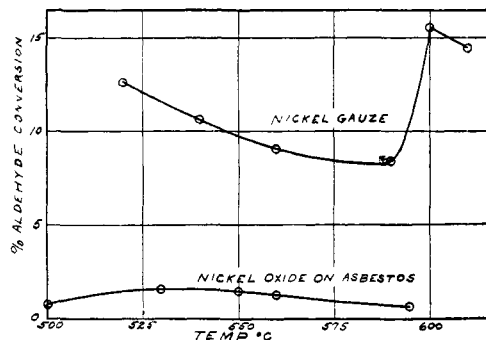


Figure 7—Conversion of Aldehyde from Oxidation of Methanol, Using Nickel as Catalyst

Data on acetaldehyde conversions using nickel as a catalyst have not been previously reported. Of course this is expected, since nickel is such a poor catalyst for this reaction.

The aldehyde conversions obtained by oxidation of methanol were not so high as some previously reported. Nevertheless, in each case studied the catalyst form giving the best heat transfer gave the best conversions. It was to be expected, however, that the conversions obtained from methanol oxidation would not be so high as those previously reported, since optimum conditions of bath temperature and catalyst length were purposely avoided. It was thought that a comparison of different forms of a catalyst operating under unfavorable conditions as well as favorable conditions (as was the case in ethyl alcohol oxidation) would more severely test the premise that the form with best heat transfer would give the highest conversions to aldehyde.

Tables I and II and also Figures 2-7 show that in all cases the catalyst with best heat transfer gives the highest conversions of aldehyde.

Summary

A laboratory apparatus has been developed for catalytic vapor-phase oxidations by means of which duplicable results may be easily obtained in a shorter time than by any other apparatus tried.

It has been found that that form of a catalyst which has the greatest coefficient of heat transfer gives the highest conversions of aldehyde from alcohol in vapor-phase oxidation.

Table II—Results of Oxidation of Methanol
Thermostat 36° C., length of catalyst 45 mm.

CATALYST	Flow Liter/min.	TEMP. ° C.	CONVERSIONS		
			Aldehyde %	CO ₂ %	CO %
Silver gauze	0.49	395	41.6	29.0	None
	0.66	433	46.0	29.2	None
	0.74	445	48.1	31.0	None
	0.89	460	60.0	27.3	None
	0.91	470	47.5	27.0	None
	0.92	480	38.3	23.2	None
Silver oxide on asbestos	0.37	455	45.2	27.5	None
	0.43	475	56.7	22.3	None
	0.57	495	53.2	22.6	None
	0.75	530	46.3	22.7	0.7
	0.89	580	39.3	23.0	5.8
Copper turnings	0.52	400	44.5	19.1	None
	0.57	410	45.2	19.0	None
	0.62	420	45.7	19.5	None
	0.74	450	45.7	18.0	None
	0.88	470	45.0	18.5	None
Copper oxide on asbestos	0.48	450	28.0	40.7	None
	0.65	480	31.1	40.0	None
	0.68	520	35.4	38.3	None
	0.69	540	38.3	31.9	None
	0.72	570	43.6	31.5	None
	0.80	610	37.0	36.6	None
Nickel gauze	0.34	520	12.6	14.8	30.0
	0.40	540	10.7	18.2	12.6
	0.48	560	9.1	25.4	14.9
	0.65	590	8.3	26.7	33.2
	0.72	600	15.6	14.6	59.6
	0.74	610	14.6	19.6	65.3
Nickel oxide on asbestos	0.54	500	0.8	26.6	26.7
	0.57	510	1.2	13.3	30.6
	0.58	530	1.5	32.4	28.1
	0.68	550	1.6	32.8	36.0
	0.71	560	1.3	29.4	44.6
	0.75	595	0.7	26.2	36.3

Higher yields of acetaldehyde have been obtained with both copper and silver catalysts than have been reported previously by investigators on vapor-phase catalytic oxidation of ethyl alcohol.

Acknowledgment

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Literature Cited

- (1) Adkins and Petersen, *J. Am. Chem. Soc.*, **53**, 1514 (1931).
- (2) Blank and Finkenbeiner, *Ber.*, **39**, 1327 (1906).
- (3) Kamm, "Qualitative Organic Analysis," pp. 139-40, Wiley, 1922.
- (4) Kingscott and Knight, "Methods of Quantitative Organic Analysis," p. 245, Longmans, 1914.
- (5) Lowdermilk and Day, *J. Am. Chem. Soc.*, **52**, 3535-45 (1930).
- (6) Mellor, "Comprehensive Treatise of Theoretical and Inorganic Chemistry," Vol. III, p. 376, Longmans, 1923.
- (7) Moureu and Mignonac, *Bull. soc. chim.*, **29**, 88 (1921).
- (8) Parsons, *J. IND. ENG. CHEM.*, **11**, 545 (1919).

Spraying Orange Trees with Lead Arsenate Alters Fruit—Oranges produced by trees sprayed with lead arsenate not only differ in chemical composition from normal oranges but they have a considerably lower vitamin C content than oranges from trees not so sprayed, according to E. M. Nelson and H. H. Mottern of the Bureau of Chemistry and Soils. Doctor Nelson has completed a series of experiments which have demonstrated that besides causing a considerable loss of vitamin C, spraying with lead arsenate reduces the acidity of the juice and decreases the sucrose, with a corresponding increase in invert sugar. The principal orange-producing states have laws prohibiting the use of arsenical sprays on this crop. Spraying oranges with lead arsenate involves no danger from arsenic poison, according to the bureau.

The investigation also showed that processing oranges by the heat method used by the Plant Quarantine and Control Administration to destroy larvae of the Mediterranean fruit fly did not change the character of the sugars, citric acid, or vitamin C content of the fruit.