Catalytic Oxidation of Ethyl Alcohol

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HE catalytic oxidation of ethyl alcohol in the vapor phase has been the subject of a large number of investigations. In the published work, the greater part of which is found in the patent literature, copper or silver has been employed most frequently. Little work has been reported where promoted catalysts were used, and there is no published work on the catalytic vaporphase oxidation of ethyl alcohol under pressure.

The catalytic oxidation of ethyl alcohol in the vapor phase over a silver catalyst has been studied at pressures of from 1 to 50 atmospheres, and at 1 atmosphere over silver catalysts promoted with samarium oxide. It has been shown that the total conversion decreases rapidly with increase in pressure. The promoted catalysts have the advantage of increasing the process yields of acetaldehyde and permitting efficient operation at a somewhat lower temperature than the unpromoted catalyst.

The purpose of this investigation was twofold: (1) to obtain quantitative data on the effect of pressure on the oxidation of ethyl alcohol; and (2) to study the oxidation at atmospheric pressure under rigidly controlled conditions, so that the variables catalyst temperature, space velocity, and ratio of oxygen to alcohol could be varied independently.

Senderens (7) from a series of qualitative studies of the oxidation of ethyl alcohol over catalysts composed of metal turnings, concluded that silver was the most suitable. Day (2) has shown that silver on pumice and silver, promoted with small amounts of rare earth oxides on pumice, were suitable catalysts for the oxidation of ethyl alcohol. They were therefore chosen for this work. Silver has the advantage over copper of being less destructive to the reaction products. It has been claimed, however, that silver becomes poisoned more readily; this would lower its efficiency and render it less useful over a long period of time. From the present investigation it would appear that silver is not as readily poisoned as is commonly assumed. In the course of this work, even without careful purification of the air used, there was no indication that the catalyst efficiency decreased.

The catalytic oxidation of alcohols to aldehydes is a coupled reaction (4). The reaction is a combination of two distinct

steps; the dehydrogenation of the alcohol to aldehyde, followed by the partial or complete oxidation of the hydrogen formed in the first step, the latter furnishing the energy necessary to maintain the reaction.

From a consideration of the principles of LeChatelier, it was expected that the initial reaction

 $C_2H_5OH = CH_3CHO + H_2$

would be inhibited by increase in pressure, while the second step.

 $2H_2 + O_2 = 2H_2O$

would be aided. As there are no available data on the effect of pressure on the free energy changes in this reaction, there was no way of definitely pre-



FIGURE 1. APPARATUS FOR PRESSURE WORK

dicting the effect. Assuming the change in pressure-volume constant to be the predominating factor, a decrease in acetaldehyde formation was to be expected with increase in pressure. It has been previously shown (1) that acetaldehyde can be condensed under pressure to ethyl acetate. It was thought that under pressure the reaction products might be less likely to undergo decomposition, so that the decrease in aldehyde formation would be partially or com-

pletely compensated for by this and by possible ester formation. The results of this study definitely show that the yields of acetaldehyde from the oxidation of ethyl alcohol drop off so rapidly with increase in pressure as to make the preparation of ethyl acetate in this manner impracticable.

High space velocities were used throughout the work in order to avoid, as far as possible, decomposition of the aldehyde formed. It was possible to do this in the metal apparatus used, since even at the high space velocities the catalyst temperature could be controlled by the rate at which heat was conducted from the catalyst by the metal walls.

OXIDATION EXPERIMENTS

Figure 1 shows diagrammatically the apparatus used in the pressure work:

The compressed air entered the system through the valve, V_{i} , the maximum basis wide open during pressure operation. The which was kept wide open during pressure operation. The alcohol was vaporized, under full operating pressure, from the vaporizer, A, and mixed with the incoming air at X. The rate of vaporization was controlled by the current through five space heaters distributed uniformly around the periphery of the The unit was mounted in a transite box filled with vaporizer. powdered magnesia to reduce heat loss. A thermocouple set in the lower end of the vaporizer served for temperature measurements. For each pressure studied, the current through the

heaters necessary for various rates of alcohol vaporization was determined by blank runs. Valves V_5 and V_6 and mixing cross X were contained in a transite box for protection againstair currents. The vaporized alcohol was prevented from condensing by a small heating coil mounted on value V_6 .

The air-alcohol mixture from X entered the top of the reaction chamber, B, the inside dimensions of which were 15.24 cm. \times 15.9 mm. The outside diameter of the thermocouple well was 8.35 mm. The catalyst occupied a space 2.25 cm. in length. The constructional details of the catalyst chamber are shown in

Figure 2. The reaction temperature was measured by means of a noble metal couple which could be moved up and down in the thermocouple well. In all cases the recorded reaction temperature was the highest temperature found.

The products leaving the reaction chamber were rapidly cooled in the condensing coil and trap, C, the latter being surrounded by cooling water. The liquid products were retained in the trap and drawn off when desired through V_3 . The pressure of the system was indicated by gage G. The gas and uncondensed vapor passed out of the trap and were expanded to atmospheric pressure through valve V_4 , by means of which the exit flow was controlled. It was found impossible to obtain a meter for the measurement of the inlet air under pressure, so that the latter had to be calculated from the measured exit flow and the analysis of the products.



CHAMBER

From V_4 onward all connections were of glass. The orifice meter, O, was used to indicate small fluctuations in flow and no attempt was made to calibrate it.

The outcoming gas, after passing through O, was scrubbed in the absorbers, D, which contained water and were surrounded by an ice bath. The by-pass F was provided so that, when conditions were being adjusted, the gas would not pass through the absorbers. L was connected to a small blower for flushing out the absorbers at the conclusion of a run. Composite samples of the scrubbed gas were taken for analysis at E. The rate of gas flow was accurately measured by means of the wet-test meter, T.

In preparation for a run the vaporizer was heated with valves V_{δ} and V_{δ} closed and the regulator wasset at the desired pressure, V_1 being open. When the vaporizer reached the operating temperature, V_{δ} was

temperature, V_4 was opened and the heating current to the vaporizer adjusted. With valve V_4 set to give the required exit flow, the reaction chamber was rapidly heated. When reaction started, as indicated by the

internal thermocouple, the heating unit of the reaction chamber was adjusted to maintain the desired temperature. For operation at atmospheric pressure, the condenser coil and trap C were removed and replaced by a glass coil condenser and glass trap. The gas outlet of the trap was connected directly to orifice meter O, cutting out gage G and expansion valve V_4 . The flow of air under these conditions was controlled by building up a small pressure by means of the regulator and expanding to atmospheric pressure through V_4 .

When steady operation conditions had been attained, the condenser trap was drained, and at the same time the exit gas was turned through the absorbers. After sufficient gas had passed through the absorbers to flush out the air, the withdrawal of a gas sample was started and so timed that it was collected at a uniform rate throughout the duration of the run.

During the run of 50 minutes the operating conditions were kept constant. In each run the hottest part of the catalyst bed was located and the internal thermocouple kept at this point throughout the run. At the conclusion of the run the condensate was drawn off and the exit gas again by-passed around the absorbers.

Acetaldehyde was determined on an aliquot of the diluted sample by Ripper's method (6). Check results within 1.0 per cent were obtained on duplicate samples.

Acetic acid was determined by titrating a measured amount of standard potassium hydroxide solution with the diluted sample in the presence of barium chloride (for the removal of carbon dioxide), using phenolphthalein as the indicator.

Unchanged ethyl alcohol was determined by the method of Peters and Baker (5) on the undiluted sample. The col-

umn was 102 cm. in length and 16 mm. in inside diameter, packed with glass rings 7 mm. in diameter and 7 mm. long. It was vacuum-jacketed throughout its length. Reflux was controlled by the rate of water flow through a dephlegmator in the top of the column.

The distillate was collected in two fractions. The first acetaldehyde was discarded; the second, the alcohol-ester fraction, was retained for the estimation of ethyl acetate. This fraction, when corrected for the ethyl acetate present, was taken as unchanged ethyl alcohol. This method gave check results within 0.3 cc. on 100-cc. prepared samples.

For the determination of ethyl acetate the alcohol-ester fraction was diluted in a suitable volumetric flask, and an aliquot was taken and refluxed for 2 hours with normal potassium hydroxide solution. The excess potassium hydroxide was then titrated conductimetrically, correction being made for acetic acid in the fraction.

The gas sample was analyzed in a Bureau of Mines modified Orsat apparatus. The accuracy obtained was within 0.1 per cent on duplicate 100-cc. samples.

The catalysts used throughout this work were prepared in \cdot the manner used by Day (2). Silver deposited on 12-mesh pumice was used for all the pressure work. For the work at 1 atmosphere, silver on pumice and silver promoted with 0.27 and 0.14 per cent of samarium oxide, respectively, on pumice were used.



FIGURE 3. EFFECT OF PRESSURE AT 360° TO 370° C.

Runs were made at 1, 3, 10, 25, and 50 atmospheres pressure. Preliminary to the runs at each pressure, blank runs were made to determine the rate of alcohol vaporization corresponding to various values for the current through the heating coils of the vaporizer. This was done by operating under conditions as near those of actual operation as possible, except that the reaction chamber was kept just hot enough to pre-vent condensation of the alcohol. The vaporizer was slowly heated until alcohol began to collect in the trap, and the heat input was maintained constant until a steady rate of alcohol flow resulted. The heat input was then increased and the procedure repeated. This was continued until the desired range of alcohol rates had been covered. These measurements were checked by determining the amount of alcohol vaporized. Nine hundred cubic centimeters of alcohol were charged into the vaporizer at the beginning of the preliminary runs, and at the end of each run the loss from the vaporizer was checked against the condensate collected. The maximum discrepancies were never more than 7 and were generally less than 5 cc.

Since, in making a run, at least an hour was required to obtain steady conditions and more time was required to cool down, it was impossible to measure directly the alcohol passed over the catalyst during the run proper. Hence it was necessary to calculate this from the products obtained.

	OXYGEN/ALCOHOL C2H5OH CONVERTED TO:								TOTAL CON- EFFI			
Темр.	In	Out	hyde	Acid	$\rm CO_2$	CO	carbons	H_2^a	VERSION	CIENCY		
• 0	$Moles O_2/mole$		07.	07.	07.	07.	07		07.			
υ.	0211	2011	/0						70			
319 322 323	$0.691 \\ 0.712 \\ 0.389$	$\begin{array}{c} 0.011 \\ 0.110 \\ 0.005 \end{array}$	$45.1 \\ 37.0 \\ 37.2$	1.8 2.7 1.6	6.4 11.4 3.0	12.3 6.7 10.7	4.5 2.2 3.4	$\begin{array}{c} 0.036 \\ 0.067 \\ 0.027 \end{array}$	$70.1 \\ 60.0 \\ 55.9$	$\begin{array}{c} 62.9 \\ 61.7 \\ 66.7 \end{array}$		
328 328 329 330	$\begin{array}{c} 0.192 \\ 0.608 \\ 0.305 \\ 0.571 \end{array}$	$0.004 \\ 0.046 \\ 0.004 \\ 0.000$	$31.7 \\ 36.0 \\ 45.7 \\ 48.4$	$1.3 \\ 2.3 \\ 1.3 \\ 2.4 \\ 2.4$	$0.5 \\ 9.9 \\ 1.4 \\ 6.3$	$1.8 \\ 5.1 \\ 6.7 \\ 10.6$	$1.4 \\ 3.1 \\ 2.6 \\ 3.2 \\ $	$\begin{array}{c} 0.072 \\ 0.166 \\ 0.154 \\ 0.151 \end{array}$	$36.7 \\ 56.4 \\ 57.7 \\ 70.9$	86.9 63.8 79.2 68.2		
331	0.139	0.004	28.9	0.6	1.0	1.3	0.8	0.097	32.8	88.7		
10 ATMOSPHERES PRESSURE												
282 314 318 321 323 324 326 330 342 347 348 370	$\begin{array}{c} 0.385\\ 0.484\\ 0.369\\ 0.327\\ 0.458\\ 0.321\\ 0.321\\ 0.351\\ 0.449\\ 0.238\\ 0.463\\ 0.374\\ 0.261\\ 0.386\end{array}$	$\begin{array}{c} 0.020\\ 0.041\\ 0.007\\ 0.038\\ 0.302\\ 0.008\\ 0.023\\ 0.122\\ 0.147\\ 0.046\\ 0.005\\ 0.013\\ 0.297 \end{array}$	$\begin{array}{c} 19.4\\ 20.3\\ 22.5\\ 26.3\\ 32.5\\ 20.8\\ 22.3\\ 22.3\\ 22.6\\ 25.6\\ 27.4\\ 27.0\\ 27.0\\ \end{array}$	$\begin{array}{c} 0.3\\ 1.1\\ 0.7\\ 1.7\\ 1.0\\ 1.3\\ 1.5\\ 1.1\\ 0.6\\ 1.0\\ 0.8\\ 1.0\\ 0.5\end{array}$	3.5 4.95 2.3 1.991 3.15 3.02 3.22 1.4	$27.3 \\ 13.3 \\ 10.0 \\ 9.3 \\ 7.2 \\ 10.3 \\ 10.7 \\ 9.1 \\ 1.3 \\ 16.2 \\ 11.2 \\ 4.4 \\ 2.9 $	11.6 2.5 3.6 6.3 6.2 4.8 0.0 0.8 7.7 8.9 2.3	$\begin{array}{c} 0.207\\ 0.139\\ 0.189\\ 0.100\\ 0.020\\ 0.127\\ 0.138\\ 0.099\\ 0.39\\ 0.39\\ 0.198\\ 0.233\\ 0.188\\ 0.191 \end{array}$	$\begin{array}{c} 63.1\\ 41.9\\ 43.3\\ 40.1\\ 44.0\\ 53.1\\ 42.4\\ 37.1\\ 26.1\\ 52.5\\ 50.3\\ 42.3\\ 35.9\end{array}$	30.7 48.4 52.3 56.2 60.0 61.2 49.0 60.2 87.2 45.0 50.6 64.8 75.0		
25 ATMOSPHERES PRESSURE												
210 255 262 308 310 329 320 321 326 349 349 349 370 389 434	$\begin{array}{c} 0.573\\ 0.770\\ 0.198\\ 0.996\\ 0.727\\ 0.701\\ 0.334\\ 0.222\\ 0.443\\ 0.248\\ 0.382\\ 0.420\\ 0.324\\ 0.386 \end{array}$	$\begin{array}{c} 0.481\\ 0.047\\ 0.093\\ 0.357\\ 0.054\\ 0.189\\ 0.048\\ 0.032\\ 0.053\\ 0.003\\ 0.042\\ 0.026\\ 0.132\\ 0.012\\ \end{array}$	1.37.69.910.913.39.313.811.214.49.911.114.811.015.0	$\begin{array}{c} 0.1 \\ 0.4 \\ 0.6 \\ 1.3 \\ 1.4 \\ 0.9 \\ 1.0 \\ 0.8 \\ 1.2 \\ 0.5 \\ 0.7 \\ 0.5 \\ 0.4 \end{array}$	$\begin{array}{c} 0.4\\ 0.2\\ 1.5\\ 16.5\\ 3.1\\ 5.5\\ 2.0\\ 1.8\\ 2.7\\ 3.4\\ 2.9\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 19.5\\ 2.0\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 10\\ 1$	$\begin{array}{c} 0.2 \\ 0.3 \\ 4.8 \\ 15.5 \\ 12.7 \\ 27.6 \\ 7.2 \\ 12.3 \\ 1.9 \\ 22.4 \\ 15.0 \\ 15.9 \\ 12.8 \\ 15.4 \end{array}$	$\begin{array}{c} 0.20\\ 0.80\\ 0.00\\ 15.00\\ 8.30\\ 9.10\\ 3.10\\ 1.00\\ 6.40\\ 14.70\\ 14.50\\ 9.70\\ 6.30\\ 5.90 \end{array}$	$\begin{array}{c} 0.010\\ 0.005\\ 0.015\\ 0.078\\ 0.085\\ 0.092\\ 0.119\\ 0.026\\ 0.067\\ 0.014\\ 0.089\\ 0.160\\ 0.015\\ 0.164 \end{array}$	$\begin{array}{c} 2.7\\ 10.0\\ 18.6\\ 60.6\\ 39.6\\ 53.2\\ 28.3\\ 27.9\\ 50.6\\ 42.8\\ 45.0\\ 50.6\\ 39.6\end{array}$	50.4 77.1 53.1 18.1 33.6 17.6 56.0 40.2 51.8 19.8 25.9 32.8 21.8 37.9		
50 ATMOSPHERES PRESSURE												
330 332 334 336 350 352 352 371 398 409	$\begin{array}{c} 0.281 \\ 1.043 \\ 0.258 \\ 0.271 \\ 0.211 \\ 0.192 \\ 0.411 \\ 0.804 \\ 0.941 \\ 0.172 \end{array}$	$\begin{array}{c} 0.104 \\ 0.489 \\ 0.100 \\ 0.091 \\ 0.029 \\ 0.095 \\ 0.254 \\ 0.187 \\ 0.146 \\ 0.105 \end{array}$	9.0 8.0 10.3 10.4 8.9 10.2 11.0 3.4 5.9 7.2	$\begin{array}{c} 0.8 \\ 0.8 \\ 0.6 \\ 0.5 \\ 0.4 \\ 0.6 \\ 0.2 \\ 0.2 \end{array}$	$2.5 \\ 12.8 \\ 1.6 \\ 2.6 \\ 3.4 \\ 1.2 \\ 2.0 \\ 16.2 \\ 12.4 \\ 1.4$	7.3 6.7 7.4 7.0 7.3 4.9 26.0 35.7 4.2	$\begin{array}{r} 4.4\\ 21.5\\ 5.7\\ 7.4\\ 6.0\\ 4.9\\ 8.8\\ 15.4\\ 24.3\\ 3.0\end{array}$	$\begin{array}{c} 0.062\\ 0.355\\ 0.032\\ 0.059\\ 0.213\\ 0.136\\ 0.108\\ 0.395\\ 0.450\\ 0.024 \end{array}$	$\begin{array}{c} 25.7\\ 52.5\\ 26.9\\ 29.4\\ 27.1\\ 32.4\\ 32.7\\ 61.8\\ 80.0\\ 16.4 \end{array}$	35.0 15.3 35.0 35.2 32.8 45.6 33.5 5.5 7.3 43.4		

^a Moles H₂ in exit gas per mole of inlet alcohol.

TABLE II. EFFECT OF CATALYSTS AT ONE ATMOSPHERE PRESSURE

	OXYGEN,	ALCOHOL	-C2Hs	OH Con	VERTED	то:—		TOTAL	France	
Темр.	In	Out	hyde	acid	$\rm CO_2$	CO	H_2^a	VERSION	CIENCY	
° C.	$Moles \ C_2H_5$	O₂/mole OH	%	%	%	%		%		
			S1	LVER C	ATALYST					
$\begin{array}{c} 308\\ 326\\ 342\\ 352\\ 363\\ 363\\ 363\\ 363\\ 363\\ 391\\ 392\\ 391\\ 392\\ 400\\ 403\\ 421\\ 4221\\ 4223\\ \end{array}$	$\begin{array}{c} 0.457\\ 0.506\\ 0.746\\ 0.834\\ 0.405\\ 0.684\\ 0.770\\ 1.082\\ 0.676\\ 0.467\\ 0.586\\ 1.014\\ 0.419\\ 0.430\\ 0.600\\ 0.408\\ 0.439\\ 0.4255\\ 0.760\\ 1.255\\ \end{array}$	$\begin{array}{c} 0.028\\ 0.146\\ 0.009\\ 0.014\\ 0.049\\ 0.164\\ 0.258\\ 0.028\\ 0.028\\ 0.031\\ 0.119\\ 0.160\\ 0.027\\ 0.144\\ 0.080\\ 0.055\\ 0.142\\ 0.060\\ 0.055\\ 0.142\\ 0.060\\ 0.055\\ 0.142\\ 0.060\\ 0.055\\ 0.002\\ 0.002\\ 0.000\\ 0.$	$\begin{array}{c} 50.6\\ 59.7\\ 53.8\\ 9\\ 64.8\\ 57.4\\ 51.6\\ 6\\ 72.1\\ 72.6\\ 63.4\\ 73.4\\ 66.2\\ 64.4\\ 73.4\\ 66.2\\ 64.4\\ 73.4\\ 66.2\\ 66.9\\$	0.82 1.22 2.23 2.23 2.21 2.14 2.23 2.23 2.15 2.14 2.23 2.23 2.23 2.23 2.23 2.23 2.23 2.2	$\begin{array}{c} 7.8\\ 5.9\\ 17.9\\ 5.2\\ 17.4\\ 11.5\\ 16.0\\ 9.7\\ 3.7\\ 3.7\\ 1.6\\ 5.5\\ 6.5\\ 5.5\\ 11.6\\ 20\\ 6\end{array}$	1.601.087.221.284.495.0030.351.743.470.0	$\begin{array}{c} 0.133\\ 0.013\\ 0.212\\ 0.122\\ 0.070\\ 0.127\\ 0.0\\ 0.127\\ 0.082\\ 0.167\\ 0.082\\ 0.146\\ 0.224\\ 0.008\\ 0.140\\ 0.084\\ 0.069\\ 0.054\\ 0.05$	$\begin{array}{c} 60.8\\ 67.8\\ 75.2\\ 73.7\\ 75.6\\ 879.1\\ 86.7\\ 85.3\\ 81.9\\ 86.3\\ 81.9\\ 77.0\\ 86.3\\ 80.7\\ 86.3\\ 80.7\\ 80.5\\ 77.0$	83.4102859348824500138876.001388576.0013885765934882455985593488245500138857455000138574550000000000000000000000000000000000	
	0.000	SILVER +	0.27 PER	CENT SA	MARIUM	OXIDE (CATALYST	0110	00.0	
355 355 370 371 379 380 394	$\begin{array}{c} 0.426\\ 0.456\\ 0.506\\ 0.634\\ 0.696\\ 0.424\\ 0.808 \end{array}$	$\begin{array}{c} 0.025\\ 0.031\\ 0.043\\ 0.048\\ 0.034\\ 0.013\\ 0.050\\ \end{array}$	$\begin{array}{r} 68.2 \\ 70.7 \\ 74.6 \\ 71.1 \\ 78.6 \\ 72.6 \\ 74.1 \end{array}$	2.2 2.4 2.6 2.2 2.6 2.1 2.8	11.2 11.9 8.5 10.1 9.7 6.2 16.9	4.0 1.7 1.8 2.2 2.8 1.6 3.6	$\begin{array}{c} 0.027\\ 0.050\\ 0.020\\ 0.030\\ 0.000\\ 0.034\\ 0.007\\ \end{array}$	85.6 86.7 87.5 85.6 93.7 82.5 97.4	78.881.585.383.083.988.076.1	
		silver +	0.14 PER	CENT SA	MARIUM	OXIDE (CATALYST			
359 385 388 392 398 411	$\begin{array}{c} 0.388 \\ 0.510 \\ 0.410 \\ 0.627 \\ 0.663 \\ 0.473 \end{array}$	$\begin{array}{c} 0.042 \\ 0.068 \\ 0.022 \\ 0.056 \\ 0.023 \\ 0.035 \end{array}$	70.5 72.8 71.9 77.7 78.1 77.0	2.4 2.2 2.2 2.5 2.1 2.8	8.1 9.2 9.7 6.4 4.0	1.7 2.4 0.8 0.1 2.0	$\begin{array}{c} 0.051 \\ 0.051 \\ 0.053 \\ 0.117 \\ 0.110 \\ 0.049 \end{array}$	82.7 85.9 86.2 87.4 84.9 92.6	85.3 85.0 83.5 89.2 92.0 83 2	

^a Moles H₂ in exit gas per mole of inlet alcohol.

This was done by means of a "carbon balance" on the products. In all cases the value so obtained checked reasonably well with the rates determined in the blank runs.

The alcohol used throughout all the work was the constant-boiling, 95.45 per cent (by weight) alcohol. In all calculations corrections were made for the water content of the alcohol.

Certain terms used in the discussion of the work may bear definition: "Total conversion" is self-explanatory, being the total alcohol oxidized expressed as a percentage of the total alcohol passing over the catalyst. "Yield efficiency" is the ratio of the alcohol converted to acetaldehyde to the total alcohol oxidized. "Oxygen/alcohol ratio" is expressed as the ratio of the gram molecules of oxygen to the gram molecules of alcohol passed over the catalyst; for the stoichiometric conversion of the alcohol to acetaldehyde the oxygen/ alcohol ratio is 0.5.

DISCUSSION

Table I includes the more important data on the pressure runs, while Table II includes those for the work at one atmosphere. Those runs in which all the products were not accounted for and those in which the catalyst showed signs of loss of activity, as well as duplicate runs, have been omitted for the sake of brevity. As previously mentioned, high total space velocities, from 25 to 30 liters of charge per hour per cc. of catalyst corrected to normal temperature and pressure, were used throughout the work.

Comparison of the tables shows that the aldehyde yields decreased with increase in pressure (Figure 3). Preliminary work showed that at one atmosphere the aldehyde obtained was decreased somewhat by increasing the length of the catalyst. This is equivalent to increasing the contact time with the catalyst after the primary reaction is over. Other conditions being the same, this would indicate that the decrease in aldehyde obtained was caused by secondary reactions which, in turn, are dependent on contact time. Since the contact time is directly proportional to the pressure at any given space velocity, it may be assumed that the decrease in aldehyde (with increase in pressure) was due to increased contact time. However, with increasing pressure, other conditions (temperature and space velocity) being equal, the amounts of unconverted alcohol recovered markedly increased (shown by "total conversions" in Tables I and II). This definitely indicates that increase in pressure decreases the rate of the primary reaction (dehydrogenation) in spite of the increase in contact time. Thus there are two important factors affecting the aldehyde yields: (a) effect of contact time on secondary reactions and (b) effect of pressure on the primary reaction.

With increasing pressure the effluent gas showed a steady increase in hydrogen content even when operating above the theoretical ratio of oxygen to alcohol. The data also appear to indicate that the percentage hydrogen increases with temperature. This is probably due to the increased contact time.

At one atmosphere and considerably shorter contact times (other conditions being the same), decomposition was less, and the hydrogen formed was not a function of the temperature within the range studied.

It will be noted that the percentage of the alcohol converted to hydrocarbons, chiefly methane, increased with increase in pressure. The chief source of hydrocarbons was the decomposition of acetaldehyde. It is probable that the decomposition is facilitated by increase in contact time. Since at atmospheric pressure the percentage of hydrocarbons in all cases was negligible, they are not included in Table II.

'At atmospheric pressure the maximum process yields were obtained at about the theoretical ratio of oxygen to alcohol and at about 415° C. On the other hand, the yield efficiency decreased steadily with increase in ratio and reached a maximum at a temperature of about 370° C.

With the promoted catalysts an increase of from 3 to 4 per cent in the process yields was obtained, slightly better yields being obtained in the case of the silver promoted with 0.27 per cent of samarium oxide than with the one containing 0.14 per cent. Only a slight improvement in the yield efficiency was obtained with the promoted catalysts.

In applying the reaction to commercial practice, a ratio of oxygen to alcohol somewhat below the theoretical would probably be most desirable. In such a case the cost of recovery of unoxidized alcohol would be balanced against the loss due to the formation of carbon monoxide and carbon dioxide. It was found in this investigation that the catalyst became temporarily poisoned, owing to deposition of carbon, when operated for any length of time much below the theoretical ratio of oxygen to alcohol. It was possible to reactivate it slowly by operating with an excess of oxygen. To avoid loss of activity of the catalyst when operating over long periods of time, it would probably be desirable to operate at a ratio of oxygen to alcohol near the theoretical.

For maximum conversion, the catalyst temperature is undoubtedly the most important factor. Faith, Peters, and Keyes (3) have clearly shown the effect of temperature and time of contact on the vapor-phase oxidation of ethyl alcohol. Their results show: (1) Maximum conversion depends upon temperature; (2) at temperatures below that of maximum conversion, lower flows give the highest conversion; and (3) at temperatures above that of maximum conversion, higher flows give slightly better conversions.

For optimum operating conditions a temperature between 370° , at which maximum yield efficiency is obtained, and 415° C., the temperature of maximum process yields, should be employed. Since, with the promoted catalysts, the process yields decrease more slowly with decrease in temperature (below 415° C.), a promoted catalyst has a distinct advantage for commercial operation. The promoted catalysts also have the advantage of being less likely to undergo temporary deactivation due to operating at low ratios of oxygen to alcohol or to overheating.

LITERATURE CITED

- (1) Adkins, Folkers, and Kinsey, J. Am. Chem. Soc., 53, 2714 (1931).
- (2) Day, J. Phys. Chem., 35, 3272 (1931).
- (3) Faith, Peters, and Keyes, IND. ENG. CHEM., 24, 924 (1932).
- (4) LeBlanc and Plaschke, Z. Elektrochem., 17, 55 (1911).
- (5) Peters and Baker, IND. ENG. CHEM., 18, 69 (1926).
- (6) Ripper, Monatsh., 21, 1079 (1900); Feinberg, Am. Chem. J., 49, 87 (1913).

(7) Senderens, Ann. chim., 13, 266 (1920).

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LABORATORY OF A. D'AILLY By

Jan Rienksz Jelgerhuis

With this, No. 48 in the Berolzheimer series of Alchemical and Historical Reproductions, we add a new artist to the series. Jan Rienksz Jelgerhuis (1770-1836) who was the son and student of the Dutch artist of like name, Rienksz Jelgerhuis.

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The pharmacist appears to be doing a filtration or more properly speaking, a straining operation.

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