

# Acetaldehyde by Dehydrogenation of Ethyl Alcohol

JAMES M. CHURCH AND HANAMANT K. JOSHI<sup>1</sup>

Chemical Engineering Department, Columbia University, New York, N. Y.

In recent years, increasing amounts of acetaldehyde have been produced by the air oxidation of ethyl alcohol and now nearly equal the production from acetylene by hydration. Both processes result in a highly diluted gas reaction mixture involving a difficult recovery of acetaldehyde, in one instance from the nitrogen of the air, unreacted alcohol, and other oxidation products and in the other, from large amounts of unreacted acetylene. In contrast, the dehydrogenation of ethyl alcohol would simplify the problem of recovery, since only acetaldehyde and hydrogen are obtained as the products from the reaction. A study of suitable dehydrogenation catalysts and conditions has demonstrated the practical advantages of such a dehydrogenation process.

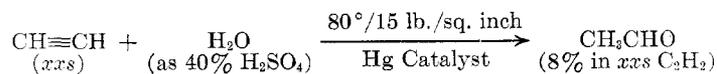
When ethyl alcohol vapor is passed over a supported

copper catalyst, containing 5% cobalt and 2% chromium as promoters, at 275° to 300° C., conversions as high as 95% with yields of 88% acetaldehyde and 10% ethyl acetate are obtained. The hydrogen by-product recovered is 99% pure and over-all losses are less than 2% of the alcohol consumed. A sustained activity of the catalyst is obtained over long periods of performance with little loss in efficiency by periodic reactivations.

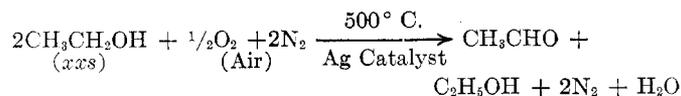
The proposed dehydrogenation method offers several advantages over present processes for the manufacture of acetaldehyde—namely, a reaction mixture rich in product for a simple recovery; a by-product hydrogen of high purity; ethyl acetate as a concomitant product in low yield; and a combined yield of 98% of valuable products with high conversions of ethyl alcohol per pass.

FOR many years acetaldehyde has been one of the most important intermediate aliphatic chemicals serving as the raw material for the production of acetic acid, acetic anhydride, ethyl acetate, butyraldehyde, *n*-butanol, pentaerythritol, and many other products. Its production in this country since 1930 has increased nearly 100-fold, with a reported production in 1948 (32) of 425,000,000 pounds. The major part of the annual production of acetaldehyde is derived from acetylene, although in recent years the air oxidation of ethyl alcohol has produced a considerable amount of acetaldehyde, with nearly 200,000,000 pounds estimated from this source during 1949 (29); it is also obtained in smaller amounts as one of the products from an air oxidation of lower hydrocarbons (14). The reactions involved in the first two of these commercial processes are shown for comparison with the reaction of the dehydrogenation process under investigation in this study:

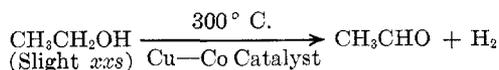
1. Hydration of Acetylene (Commercial Process)



2. Oxidation of Ethyl Alcohol (Commercial Process)



3. Dehydrogenation of Ethyl Alcohol (Proposed Process)



These equations show that the present commercial processes involve a recovery of the product from a diluted gas mixture. In the hydration of acetylene the acetaldehyde product is mixed with an excess of unreacted acetylene in a ratio of 1:12, whereas in the oxidation of ethyl alcohol the product is diluted with nitrogen, water, and excess of alcohol in a ratio of 1:4. Recovery of the acetaldehyde product in both these processes entails a difficult

and costly operation involving the absorption of the acetaldehyde in a dilute alcohol solution at low temperature followed by distillation of the absorption solution for final separation and purification. In contrast, the dehydrogenation of ethyl alcohol results in 1:1 mixture with the by-product hydrogen, and separation and recovery of the product is simplified by low temperature condensation of most of the acetaldehyde and scrubbing the hydrogen gas in dilute alcohol for remaining traces of the product.

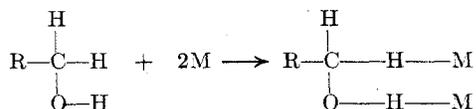
Acetaldehyde was first prepared from ethyl alcohol by Davy (7), who employed a platinum black catalyst and passed a mixture of alcohol and air over it at a low temperature. More thorough studies of the air oxidation of ethyl alcohol, employing various catalysts, were made by Kuhlman (18), Strecker (30), and Grimax (12). Not until the work of Trillatt (31) and Orloff (22) in 1902, however, were any quantitative data reported. More recently Faith and Keyes (10) carried out extensive investigations of this reaction and found that silver gauze was the best catalyst. Employing a flow rate of 0.57 liter of alcohol vapor per minute over a heated silver gauze, 12 mm. in diameter and 15 mm. long, maintaining the temperature fairly constant at 515° C., they obtained an 80.6% conversion of alcohol to acetaldehyde with losses of 13.3% to carbon dioxide and 3.2% to acetic acid. Shreve (28) and Faith, Keyes, and Clark (11) report slightly higher yields of 85 to 95% by air oxidation of ethyl alcohol to acetaldehyde by use of a silver catalyst at a temperature of 550° to 570° C. and a conversion per pass of 50 to 55%. However, Groggins (13), reporting results from a similar process, claims only 70 to 80% of the theoretical yield of acetaldehyde under identical conditions. Based on an average of the results claimed by the oxidation process—namely, 50% conversion of alcohol per pass and over-all theoretical yield of 85% of acetaldehyde—this process possesses certain inherent disadvantages compared with a similar process employing dehydrogenation instead of air oxidation. First, the presence of the water by-product, formed by removal of hydrogen by oxidation, with appreciable quantities of other oxidation products such as acetic and formic acids gives rise to serious corrosion problems in condensation and recovery of the products. Secondly, the use of air as an inexpensive oxidizing agent results in considerable dilution of the gaseous products from the reaction be-

<sup>1</sup> The National Chemical Laboratory, Darawade Bldg., Poona 4, India.

cause of large amounts of nitrogen involved. Over half the products from the oxidation reaction are noncondensable (mainly nitrogen with some carbon dioxide), making separation of the acetaldehyde product fairly difficult. Lastly, conversion of alcohol to acetaldehyde by oxidation cannot be expected to proceed without appreciable losses by further oxidation, resulting in a lower yield of aldehyde. Therefore, an investigation of the possibilities of employing dehydrogenation for converting ethyl alcohol to acetaldehyde was believed justified, as in theory at least, it was free of the disadvantages of the oxidation process. In addition, advantages such as the valuable hydrogen and ethyl acetate by-products favor the dehydrogenation reaction for commercial production of acetaldehyde from ethyl alcohol.

### THEORY OF DEHYDROGENATING ALCOHOLS

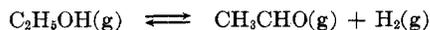
Dehydrogenation of ethyl alcohol to form acetaldehyde is an equilibrium reaction which is complicated, under certain conditions, to permit further condensation of the acetaldehyde product, forming such by-products as hydroxybutyraldehyde (aldol), ethyl acetate, and subsequent hydrogenated products due to the presence of the by-product hydrogen. Under favorable conditions for the dehydrogenation reaction, however, these side reactions may be minimized and a high yield of the acetaldehyde obtained. The theory of the dehydrogenation of alcohols has been reported (4, 24) as proceeding through the formation of a complex between the alcohol and the catalyst:



From various studies involving the catalytic dehydrogenation of alcohols, the following statements will suffice to summarize the generally accepted theories concerning this reaction:

1. The reaction follows a pseudo first-order reaction rate equation (21).
2. The energy of activation for the dehydrogenation is constant for a given catalyst but varies with the type and method of preparation of the same (21, 23).
3. The reaction rate is dependent on the temperature as stipulated by the hypothesis of Arrhenius and is consistent with the constancy of the energy of activation (21, 23).
4. The alcohol molecules are first adsorbed on the surface of the catalyst, with the hydroxyl group parallel to the surface and the rest of the molecule perpendicular to it (24).
5. The reaction velocity is independent of the pressure on the system (24).

The maximum conversion of alcohol to aldehyde is of course dependent on the equilibrium of the reaction. Various workers (1, 25, 26) have studied the equilibrium as represented by the simple dehydrogenation equation:



They report values for the per cent conversion of the alcohol from experimental data and calculated from heats of combustion and specific heat data. These results of the various equilibrium values, expressed in per cent conversion of ethyl alcohol to acetaldehyde at different temperatures, show little agreement between the experimental values and those calculated from fundamental data, as shown in Table I.

Of the various catalysts suggested for dehydrogenating alcohols, copper appears to be the most common, by itself and in combination with other catalytic materials. It appears to be fairly ideal for this reaction in that it is specific and of high activity, but it does lack stability, losing its activity quite readily (8). Many investigators have also reported the use of catalysts other than copper (2, 5, 15, 17, 20, 27). Among these catalytic materials were compounds of iron, cobalt, nickel, manganese, and zinc, somewhat in the order of their increasing dehydrogenation ef-

TABLE I. EQUILIBRIUM VALUES FOR DEHYDRATION OF ETHYL ALCOHOL

Temp., °C.	Rideal (26)		Parks and Huffman Calcd. (25)	Anderson, Beyer, and Watson, Calcd. (1)
	Exptl.	Calcd.		
150	3.9	89	5.0	23.5
200	10.6	98.3	11.5	45.5
250	38.0	99.2	21.0	70.0
275	60.2	99.7	25.2	78.5
300	..	..	33.5	85.5

iciency. Many of these, particularly in the form of their basic salts, caused decomposition and condensation of the aldehyde product; the increasing order of this tendency was indicated as manganese, iron, cobalt, and nickel. Therefore from the standpoint of alcohol conversion for a high yield of aldehyde product, these catalysts would not be desirable.

Extensive work has been done on the catalytic activity of copper in the form of pure reduced metal, mixtures of reduced metal with other materials, alloys with other metals, and reduced salts supported on inert materials. The first of these experiments with reduced copper was carried out by Sabatier and Senderens (27), who found that in a finely reduced state, copper was outstanding among the various metal catalysts studied. Palmer (23) likewise, from a study of the effect of reducing conditions, found copper metal particularly effective, with a maximum activity when prepared by reduction at low temperature. Reactivation of copper catalysts through successive oxidation and reduction also was reported (24) as showing some increase in catalytic activity, becoming constant after the third reactivation. The preparation of refined copper metal from its various salts as reported by Neish (21) indicated that the catalyst obtained by reduction of copper oxide, previously heated to 1000° C., had the highest activity.

In mixtures of reduced copper with other materials, such as oxides or carbonates of sodium, iron, zinc, manganese, and magnesium, Palmer (23) reported a decrease in catalytic activity in most cases, even with small additions of 0.5% of these materials. The addition of oxides of manganese and magnesium improved the catalytic activity of the copper initially, but the life of these mixed catalysts was short. No references could be found in the literature concerning the use of mixed copper catalysts in the form of copper alloys for the dehydrogenation of ethyl alcohol. However, copper alloys are frequently mentioned as those used in commercial processes for the production of ketones by the dehydrogenation of secondary alcohols, such as isopropyl, *sec*-butyl, and *sec*-hexyl alcohols. Various types of brasses and bronzes, containing small amounts of tin, cadmium, chromium, nickel, and magnesium, are claimed as efficient sturdy commercial catalysts for dehydrogenation purposes (23). One report (21) did include the use of a codeposit of copper with a small amount of nickel for the dehydrogenation of ethyl alcohol, but the yields were low, supposedly because of decomposition of the acetaldehyde formed.

Supporting materials increase both the life and activity of the catalyst owing to the increase in active surface area and minimization of local overheating by increase in thermal conductance of the support. Lorang (19) used both pumice and dolomite as the supports for a copper catalyst prepared by a reduction of the decomposition product from a deposition of the nitrate salt. He claimed a constant activity over a long period of dehydrogenation, especially in a combination using traces of oxides of zinc, cerium, thorium, and zirconium as promoter catalysts. Dunbar (9) also used pumice and diatomaceous earth as supports for copper using chromium as the promoter with considerable success in the dehydrogenation of higher alcohols. In contrast with unsupported copper catalysts for the dehydrogenation of ethyl alcohol, which Constable (6) reported as of high activity but of short life, Young (34) claimed a long life high activity catalyst using a silica catalyst support with a copper chromium combination.

Likewise Johnson (16) found that copper carbonate with traces of zinc and magnesium oxides supported on alumina gel catalyst gave high conversions over a long period of time, although it resulted in the formation of higher condensation products.

### APPARATUS

Figure 1 shows the apparatus designed for determining the performance characteristics of the more active catalysts. A slightly different type of apparatus was employed in preliminary evaluation tests for determining the relative efficiencies of various catalysts; it consisted of a constant feed buret for charging alcohol to

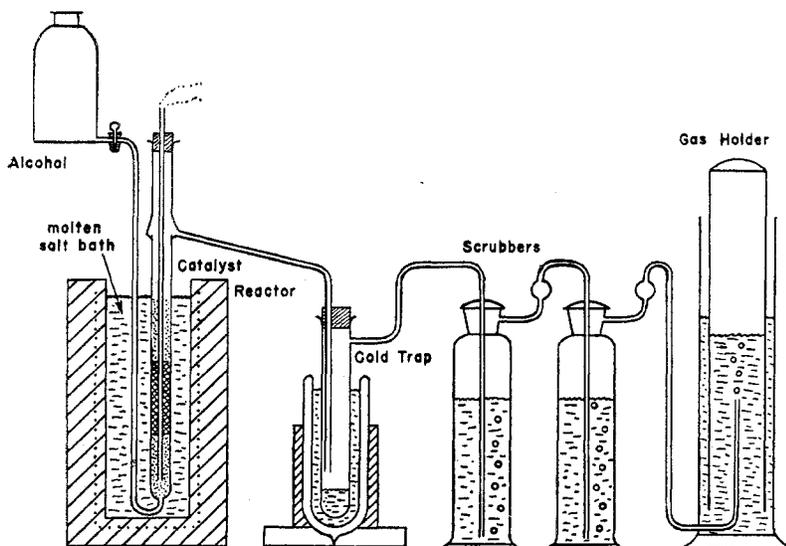


Figure 1. Dehydrogenation Apparatus

a vaporizer and a preheater, made of a horizontal 15-mm. diameter heat-resistant glass tube filled with glass wool and heated in an electric furnace to the desired temperature. The preheated alcohol vapors were then passed to a vertical 20-mm. diameter heat-resistant glass tube containing a 6-inch bed of catalyst and heated by means of an electric furnace. The temperatures of the incoming vapors and the catalyst were measured by suitable thermocouples placed in the vapor lines and the catalyst bed. The reaction products leaving the top of the reactor were chilled in an ice trap where the major part of the alcohol and aldehyde were condensed; then any uncondensed vapors were absorbed in two wash bottles containing water, and the residual gases were finally collected in an aspirator bottle for measurement.

In the performance tests the dehydrogenation apparatus was changed in order to determine the activity of the catalysts over a longer period of operation. Automatic controls were required in order to maintain constant temperatures, uniform flow of reactant, and collection of products without interruption. In this apparatus a larger graduated 5-liter bottle for charging larger quantities of alcohol replaced the buret. In place of electric furnace heaters the reactor was heated in a mixed salt bath composed of equal weight quantities of sodium and potassium nitrates contained in an electric well heater. The salt bath temperature was controlled by use of a bimetallic thermoregulator placed in series with the heating element of the well heater. An electrical condenser in parallel with the bimetallic regulator prevented sparking for better operation of the thermostat in maintaining a constant temperature within  $\pm 3^\circ \text{C}$ . A large cold trap, chilled in a dry-ice bath, condensed most of the products; the head of the reactor was designed to prevent any products partially condensed in the upper part of the tube from returning to the reactor. The reac-

tor itself consisted of a U-tube with an enlarged leg, 20 mm. in diameter, housing the 6-inch catalyst bed supported by plugs of glass wool. A traveling thermocouple was placed in a tube running through the center of the catalyst bed and supported by a stopper in the reactor head. Larger 1000-ml. gas absorption bottles were employed for complete removal of the condensable products and a large calibrated gas holder collected noncondensable products.

### PREPARATION OF CATALYSTS

Previous studies on dehydrogenating alcohols had shown copper to be the best of the catalyst materials and it was chosen as the primary catalyst material, alone and in combination with other elements. Various types of copper catalysts were prepared by a number of methods from different salts of copper with and without cocatalysts and support materials. The catalysts were divided into two groups—series A without catalyst support and series B with catalyst support. The catalyst compositions are given in Tables II and III.

One method of preparation, which was used mainly for the A series catalysts, consisted of suspending 25 grams of cupric oxide in a solution of 50 grams of cupric nitrate  $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$  dissolved in 1 liter of distilled water. A molar equivalent of 28% ammonia was added for precipitation of the cupric hydroxide. The combined precipitates were then washed thoroughly, mixed with a small amount (2 to 3%) of animal hide glue while wet, slowly dried on a steam bath, and granulated by stirring. Finally the granules were decomposed by heating over a gas flame for a few minutes and then were sieved for proper size. In the mixed catalysts the other materials, as nitrates or oxides, were added along with the cupric salts prior to precipitation. A slight modification included the use of ammonium carbonate in place of ammonium hydroxide for the precipitation of the mixed carbonates.

In another method, employed chiefly for the preparation of some of the supported catalysts, a melt or strongly concentrated

TABLE II. COMPOSITION OF UNSUPPORTED COPPER CATALYSTS

Catalyst No.	Copper Salt	Promoter Catalyst <sup>a</sup>	Mesh Size <sup>b</sup>
A-1	Oxide from pptd. hydroxide	None	8-20
A-2		5% Cr <sub>2</sub> O <sub>3</sub>	8-20
A-3		5% CoO	8-20
A-4	Metallic screen	None	No. 100 gauze
A-5	Oxide from pptd. carbonate	7% ZnO	1/16-3/16 inch spheres
A-6		5% MgO	1/16-3/16 inch spheres

<sup>a</sup> Based on weight of original copper oxide content.

<sup>b</sup> Tyler standard mesh.

TABLE III. COMPOSITION OF SUPPORTED COPPER CATALYSTS

Catalyst No.	Copper Salt	Support Material <sup>a</sup>	Promoter <sup>b</sup>
B-1	Nitrate hydrate melt	Long fiber asbestos	None
B-2		Pumice	1.62% Cr <sub>2</sub> O <sub>3</sub>
B-3		Alumina gel	None
B-4	Ammonia solution of nitrate	Pumice	5% CoO
B-5	Formate solution	Pumice	5% MgO
B-6		Pumice	5% CoO
B-7		Short fiber asbestos	5.2% CoO
B-8	Nitrate solution	Alundum	5.2% CoO
B-9		Short fiber asbestos	5.2% CoO + 1.8% Cr <sub>2</sub> O <sub>3</sub>
B-10		Short fiber asbestos	5.2% CoO + 4.4% Cr <sub>2</sub> O <sub>3</sub>
B-11		Short fiber asbestos	None

<sup>a</sup> Mesh size: Pumice 1/8 to 1/4 inch spheres; alumina 8-14 mesh; asbestos 8-20 mesh.

<sup>b</sup> Amount based on weight of original copper oxide content of catalyst.

solution of the cupric nitrate salt was used. The support material, either acid-washed asbestos fiber, pumice, or alumina granules, was added to the hot melt or solution and stirred for complete impregnation. The solution mixture was then strongly heated over a flame for subsequent evaporation of water and partial decomposition of the salts to form a granular solid mass consisting of the support material thoroughly coated with the catalytic materials. In other catalysts the freshly precipitated cupric hydroxide, with or without coprecipitated hydroxides of the promoter materials, was first dissolved in a sufficient amount of 28% ammonia solution and the support material thoroughly saturated with the solution before evaporation of the mixture to dryness. This resulted in a fairly even coating of the catalyst support with the oxides. In a modification of this procedure cupric formate solution was employed in place of the cupric ammonia solution in similar fashion, and in another a suspension of the precipitated carbonates was used in place of the hydroxides.

Of all the methods tried, the best catalysts were prepared by impregnation of the support solution in hot 25% cupric nitrate solution, with and without added promoter salts, by a long period of soaking followed by drying. The impregnated support material was finally heated at elevated temperatures approaching 400° C. in order to decompose the nitrate to form an oxide coating on the support material. Repeated impregnations, totaling six to eight, gave a heavy evenly coated catalyst of maximum activity and long life. In all catalyst preparations, reagent grade chemicals were used.

### PROCEDURES

The catalysts, prepared in the form of their oxides were charged into the reactor tube and heated for a period of 2 or more hours in a current of dry filtered air to ensure complete decomposition of the last traces of other salts. The temperature was then lowered to a little below 300° C. and a slow stream of alcohol vapor produced from 95% ethyl alcohol was passed over the catalyst for reduction of the oxides. Care was exercised during this reduction to avoid overheating of the catalyst as the reaction is exothermic. Following reduction of the catalyst, noted by the absence of moisture in the exit gases, the temperature of the catalyst bed was adjusted to the desired level, and the rate of alcohol vapor was increased to a maximum for an optimum conversion and yield of the dehydrogenated products. During the run, which lasted for several hours, the temperature was maintained within  $\pm 2^\circ$  C. of the desired temperature, and the products were collected and measured for determining the efficiency of the catalyst at any time during the run. At the end of the run, the total volume of liquid products in the condensate trap, those absorbed in the scrubber solution, and the volume of noncondensable gas in the gas holder were noted. The condensed and absorbed products were combined and made up to a known volume with distilled water. Aliquots of this product solution were analyzed for alcohol, aldehyde, acid, and ester content according to the methods described in the following section.

The amount of alcohol reacted was equivalent to the hydrogen content of the gaseous product, and therefore the percentage conversions and yields were computed on this basis. The difference

between this amount and the equivalent amount of the liquid products obtained was regarded as unaccountable loss. Thus yields could be calculated by the following expression:

$$\text{Total \% yield} = \frac{\text{moles aldehyde} + \text{ester}}{\text{moles of H}_2} \times 100$$

Likewise the percentage conversion of the alcohol was calculated from the amount of alcohol consumed in terms of equivalent amounts of hydrogen produced. In the runs for determining the efficiency of the catalyst, the change in catalyst activity was denoted in terms of the percentage alcohol reacted during a given period of time, as measured by the volume of gaseous product collected. Analysis of samples of gaseous and liquid products at short intervals during the run was sufficient to detect any change in the catalyst activity. Reactivation of the catalyst was readily achieved by stopping the alcohol vapor and passing air over the heated catalyst while maintaining the catalyst bed temperature below 400° C. for an hour or so to convert the metallic catalyst to the corresponding oxide mixture and then reducing again with alcohol vapor with the temperature maintained below 300° C. as described previously.

The products collected from the dehydrogenation consisted mainly of unreacted ethyl alcohol, acetaldehyde, ethyl acetate, acetic acid, and hydrogen. The gaseous hydrogen by-product was analyzed in an Orsat apparatus by the usual standard gas analysis method. The aqueous solution of the liquid products, prepared from the condensate and absorber solutions was analyzed for free acid by a standard alkali titration of an aliquot portion. Another sample was refluxed with an excess of standard alkali for 1 hour during which time the ester product was hydrolyzed, but subsequent condensation of the aldehyde product, which forms a colored solution, prevents a direct back titration of the alkali. Instead the solution was treated with excess standard acid; heating was continued to destroy the color; and the excess acid was back-titrated with standard alkali. Thus the amount of ester present could be calculated from the volume of standard alkali consumed.

Acetaldehyde was determined by adding an excess of standard bisulfite solution to an aliquot sample of the product solution and allowing the mixture to stand, with frequent shakings, at room temperature for 2.5 hours, according to the standard procedure for acetaldehyde (3). The sample was then made up to a known volume with distilled water, and the excess bisulfite was determined iodimetrically by titration of an aliquot with excess standard iodine solution in the cold, followed by back titration with standard sodium thiosulfate using starch-iodide as the indicator. The aldehyde-sulfite addition compound does not react with the iodine solution, and therefore the amount of aldehyde could be computed from the amount of bisulfite consumed in forming the addition compound.

### DISCUSSION OF RESULTS

A total of some fifty runs with the unsupported and supported catalysts was made to determine the efficiency of the various catalysts under varying conditions of temperature and space velocity for a maximum conversion of alcohol and yield of aldehyde. For results from the better runs, representing the optimum conditions for the catalysts under examination, see Table IV. In addition, a number of continuous performance runs, lasting from 50 to 100 hours, were made with the better catalysts. Changes in activity, in terms of initial activity, are shown in Table V. Lastly, a 100-hour run was made with one of the best catalysts with reactivation at 24-hour intervals (Table VI).

TABLE IV. PERFORMANCE OF CATALYSTS IN DEHYDROGENATION OF ETHYL ALCOHOL

Run No.	Catalyst	Temp., ° C.	Space Velocity <sup>a</sup>	% Conversion	Compn. of Liquid Products <sup>b</sup> , %				H <sub>2</sub> Gas, %
					AcH	EtAc	HAc	X <sup>c</sup>	
UNSUPPORTED CATALYSTS									
A-13	CuO-Cu(OH) <sub>2</sub> from nitrate	335	8.6	65	90	9	0.2	0.8	99.2
A-33	CuO-Cu(OH) <sub>2</sub> from nitrate + 5% CoO	330	15.7	57	88	7	0.3	4.7	93.6
A-52	CuCO <sub>3</sub> from nitrate + 7% ZnO	335	13.5	80	78	9	0.4	13.1	99.3
A-62	CuCO <sub>3</sub> from nitrate + 5% MgO	332	14.1	78	78	8	0.7	13.3	99.0
SUPPORTED CATALYSTS									
B-12	CuNO <sub>3</sub> melt (asbestos)	330	14.0	85	88	10	0.3	1.7	99
B-42	CuNH <sub>3</sub> + 5% Co (pumice)	325	25.0	68	83	10	0.9	6.1	95
B-62	Cu For 5% Co (pumice)	330	17.7	67	84	10	0.6	5.4	95
B-73	CuNO <sub>3</sub> 5% Co (asbestos)	337	17.2	94	89	7	0.6	3.4	96
B-93	CuNO <sub>3</sub> 5% Co, 2% Cr (asbestos)	330	18.0	93	83	9	1.0	7.0	95
B-113	CuNO <sub>3</sub> Soln. (asbestos)	328	18.8	79	90	8	0.9	1.2	99

<sup>a</sup> Cc. alcohol vapor/cc. catalyst bed/minute.

<sup>b</sup> Theoretical yield based on alcohol reacted.

<sup>c</sup> Mainly high boiling by-products; also includes losses.

TABLE V. CONTINUOUS PERFORMANCE OF DEHYDROGENATION CATALYSTS

Catalyst No.	A-51	B-41	B-51	B-71	B-91	B-92	B-111
	CHARACTERISTICS						
Original Cu salt	Carbonate	NH <sub>4</sub> Complex	Formate	Nitrate	Nitrate	Nitrate	Nitrate
Promoter, %	7% ZnO	5% CoO	5% MgO	5% CoO	5% CoO, 2% Cr <sub>2</sub> O <sub>3</sub>	5% CoO, 2% Cr <sub>2</sub> O <sub>3</sub>	None
Support	None	Pumice	Pumice	Asbestos	Asbestos	Asbestos	Asbestos
Reaction temp., ° C.	275	275	275	275	275	300	275
Initial conversion EtOH, %	35	44	68	55	50	72	35
Yield AcH <sup>a</sup> , %	81	85	74	90	85	84	89
Yield EtOAc, %	8.7	10.0	11.3	8.7	9.6	9.3	9.2
	CONTINUOUS ACTIVITY, % OF INITIAL ACTIVITY <sup>b</sup>						
Hours							
2	99	97	96	100	98	96	95
4	97	93	89	100	96	95	92
6	96	85	80	98	94	93	89
8	93	79	69	97	92	91	85
10	84	73	61	95	91	90	80
12	77	64	52	94	90	89	79
24	41	43	36	85	88	87	73
30	34	39	32	84	87	86	72
36	30	36	29	82	87	85	71
48	26	32	23	80	86	84	70
54	24	32	End	79	86	83	68
60	22	End		78	85	82	66
72	End			75	84	80	65
84				73	84	78	63
96				70	83	72	61
100				70	83	71	60

<sup>a</sup> Theoretical yield, based on alcohol reacted, remained unchanged with decreasing catalyst activity.

<sup>b</sup> Time required to collect 800 cc. H<sub>2</sub> gas.

TABLE VI. CONTINUOUS PERFORMANCE WITH INTERMITTENT REACTIVATION OF SPECIAL DEHYDROGENATION CATALYST

Catalyst composition (B-9): Cu from cupric nitrate solution + 5.2% CoO + 1.8% Cr<sub>2</sub>O<sub>3</sub>, impregnated on short fiber asbestos as oxides

Conditions of run:  
 Alcohol feed, 40 cc./hour; catalyst 16.2 grams (38.9 cc.)  
 Temperature, 275° C.; initial conversion EtOH, 49.6%  
 Space velocity (cc. alcohol vapor/cc. catalyst bed/minute), 16.2

Initial activity:  
 Conversion of EtOH, 49.6%  
 Yield aldehyde, 85.1%; yield ester, 9.6%<sup>a</sup>

Continuous activity: % initial activity, time required to collect 800 cc. H<sub>2</sub> gas

Hours	%	Hours	%
0	100	55	107
3	96	58	101
6	93	61	98
9	92	64	95
13	89	67	94
22	87	77	92
28	86 (Reactivated 1 hour)	80	88 (Reactivated 1 hour)
29	105	81	105
31	101	83	102
34	98	85	99
38	96	88	97
40	93	92	94
51	90 (Reactivated 1 hour)	102	91
54	88	105	88 (End of run)

<sup>a</sup> % yield, based on alcohol reacted, remained unchanged throughout run.

**Catalyst Activity.** The results obtained with the various catalysts show considerable variation in activity in terms of the percentage conversion of alcohol by dehydrogenation as well as in theoretical yield of aldehyde and other by-products. Table IV gives the results for the supported copper catalyst (run B-113), which was many times more effective than the copper catalyst used in run A-52. In general those catalysts prepared directly from soluble nitrate salts were more effective than insoluble oxides or carbonates; thus, the method of preparation contributes much to catalytic activity. Apparently catalyst activity is directly proportional to total active surface area which is much greater in freshly prepared catalysts. A comparison of activities of supported and unsupported catalysts indicated generally that supported catalysts contained greater active surface area per volume of catalyst, although the weight of actual catalyst was considerably less. The nature and type of support material likewise contributes a major effect on catalytic activity—for example, the asbestos-supported catalysts which proved superior to the pumice-supported catalysts, although the catalyst content was quite similar. The method of impregnation of the catalyst support material for a uniform and even coating of the catalyst is highly

important. A coating of asbestos fibers from a melt of copper salt, such as the catalyst used in run B-12, was less effective than the catalyst of run 113 prepared from a solution of the salt. Little difference, however, was noted in the activity of catalysts prepared from various soluble salts; this was probably because all were finally converted to corresponding oxides and therefore were fairly identical in chemical composition in the active state. The mixed catalysts, which included a promoter material, behaved quite differently from those containing only copper. Additions of cobalt as a promoter greatly increased activity and resulted in higher conversions of alcohol, as is shown by a comparison of run B-73 and run B-113, both made under almost identical conditions.

Other promoter materials did not seem to affect catalyst activity much but did alter the ratio of aldehyde yield to other by-products. The catalysts of runs A-52 and A-62, which contained alkaline oxides of zinc and magnesium, caused considerable by-product formation. Undoubtedly this was due to their basic character, which favored the conversion of the normal aldehyde product to higher condensation products. Similar results were noted in runs with catalyst B-3, employing alumina as the catalyst support; these indicated that B-3 also behaved as a condensation catalyst. As it was desirable in this study to minimize the formation of such by-products in order to increase the yield of aldehyde, such alkaline materials were not considered suitable constituents for dehydrogenation catalysts. The pure copper catalysts of runs A-13 and B-113 gave the highest yields of aldehydes with a minimum of by-products. When cobalt was added to the copper, an increase in dehydrogenation occurred with only slight losses in yield of acetaldehyde due to decomposition to gaseous by-products. However, additions of chromic oxide to the copper catalyst caused some dehydration of ethyl alcohol thus producing considerable amounts of ethylene in the gaseous by-products. The main by-product, ethyl acetate, was formed in about the same amounts with the various catalysts, and therefore its formation is probably not a function of the catalyst but rather a vapor-phase reaction of the Tischenko type.

**Stability of Catalysts.** In the performance tests with catalysts under continuous operation, activity varied greatly as the dehydrogenation reaction was continued. Furthermore, catalyst life, as determined in these runs, showed different results, in most instances, than given in previous reports on the performance of similar type catalysts. Constable (6) found that copper catalysts, prepared by various methods, all lost their activity rapidly at temperatures above 280° C. with the best of the group losing as much as 70% of initial activity at 300° C. within 2 hours. On the other hand, Johnson (16) claimed that copper catalysts containing magnesium and zinc oxides retained their activity for long times. However, the results from this study definitely demonstrated that a sustained activity could be obtained from several of the copper catalysts at temperatures in the neighborhood of 300° C. (Table V). In runs B-71, B-91, B-92, and B-111, all catalysts retained a high percentage of their initial activity over the 100 hours of the test. The reverse was true of the catalysts of runs A-51 and B-51 containing zinc and magnesium ox-

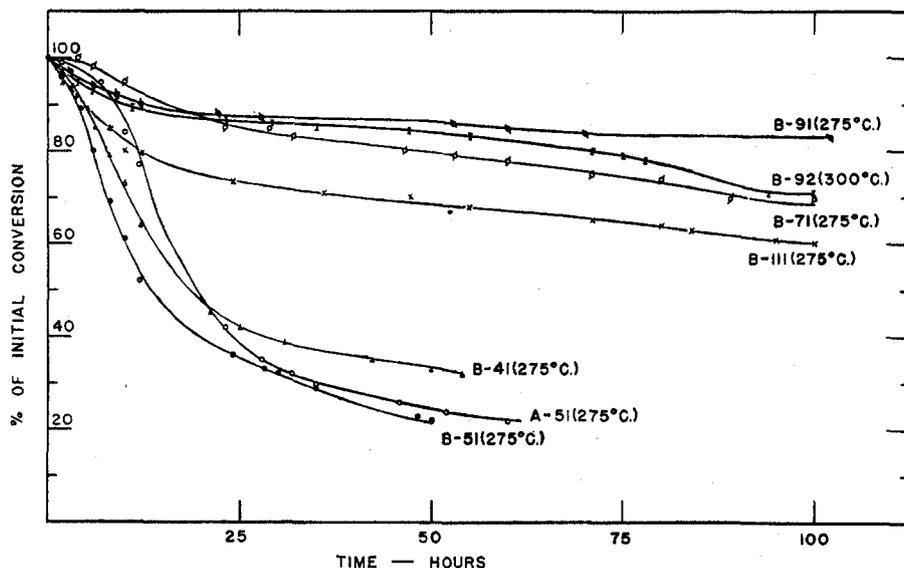


Figure 2. Continuous Performance of Catalysts

ides, respectively; these were the poorest of the group, and lost over 50% of their initial activity within 24 hours of continued dehydrogenation. Again, the type of catalyst support affected the life of the catalyst, as was noted in initial catalytic activity in these performance tests. Those catalysts containing asbestos as the support proved to have the greatest stability in terms of continued sustained activity, whereas those supported on pumice, as in runs B-41 and B-51, showed low catalyst life. The greatest contrast in this regard is shown in the results obtained in runs B-41 and B-71; the catalyst was almost identical but where pumice was used as the support in the former, asbestos was used in the latter. The changes in activity, in terms of percentage of initial activity, were 43 and 85%, respectively, after 24 hours. At the end of 48 hours the activities were 32% for the pumice as compared to 80% for the asbestos support. The uniformity obtained in impregnation and coating of the asbestos with the catalytic material not only provides a larger active surface area but one less susceptible to thermal deterioration on sustained heating at higher catalytic temperatures. The greatest sustained activity was obtained with catalyst B-9 containing both cobalt and chromium oxides. It retained over 80% of its initial activity after 100 hours of dehydrogenation at 275°C., as obtained in run B-91. With cobalt alone as the promoter ingredient with copper, the activity of catalyst B-7 after 100 hours (run B-71) at 275°C. was considerably less—70% as compared to 83% for the combined promoter under identical conditions of run B-91. This is in accord with the results reported (9, 19) from the use of chromium as a promoter with copper in the dehydrogenation of higher alcohols. The effect of increased temperature on sustained activity is shown in a comparison of runs B-91 and B-92. As might be expected the loss of activity was greatest at the higher temperature. The results of these continued performance tests are also shown in the curves of Figure 2.

**Reactivation of Catalyst.** Surprising results were obtained in the reactivation of some of the sturdier catalysts; these regained not only their initial activity but a slightly improved activity following reactivation and sustained activity at a higher level for part of the continued dehydrogenation. This is shown in the results obtained from catalyst B-9, the sturdiest and one of the most active, given in Table VI and plotted in the graph of Figure 3. At the end of 28 hours of continuous performance the catalyst had lost 14% of its initial activity, but after reactivation by a slow oxidation of the catalyst with air for 1 hour at 350° to 400°C., the activity was 105% of the initial activity. Continued dehydrogenation with the reactivated catalyst over a period of an-

other 25 hours showed another loss of activity to 88% of the initial activity. Two further reactivations increased the activity to 107 and 105% of the initial activity, with decreases to 88% after 25 hours continued dehydrogenation in both cases. Thus a sustained activity over an indefinite period, averaging 96% of the initial activity, can be expected by intermittent reactivation of the catalyst at 24-hour intervals.

#### PROPOSED COMMERCIAL PROCESS

The results of this investigation indicate that a process for the manufacture of acetaldehyde by dehydrogenating 95% ethyl alcohol is not only commercially feasible but that the dehydrogenation reaction offers several advantages over existing commercial processes employing air oxidation of ethyl alcohol or hydration of acetylene. Under the optimum conditions determined by this study, using a copper

catalyst prepared from copper nitrate solution impregnated on an asbestos support and containing 5% cobalt oxide and 2% chromium oxide, based on the weight of copper oxide equivalent, a sustained conversion of about 90% of the alcohol at 275°C. is obtained, resulting in 85% of the theoretical yield of acetaldehyde and 10% of the theoretical yield of ethyl acetate, thus representing less than 5% losses of alcohol in other by-products. In terms of pounds of products this means 89 pounds of acetaldehyde and 10 pounds of ethyl acetate per 100 pounds of catalyst each hour, an acceptable production capacity for a commercial unit.

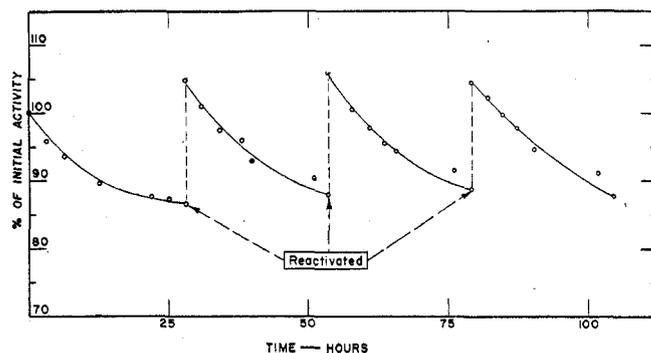


Figure 3. Reactivity of Catalyst

B-91 = Cu-Co-Cr, 275°C.

A flow sheet of the proposed commercial process is shown in Figure 4. The alcohol, which is a tax-free special denatured type (S.D.29) containing traces of acetaldehyde, is vaporized at a constant rate in an evaporator at 100°C. and preheated in a heat exchanger by the product gases to 200°C. before it enters the catalytic converters, where dehydrogenation takes place. The converters consist of a series of the conventional vertical tubular type, packed with the supported copper-cobalt-chromium oxide catalyst combination, maintained at 275° to 280°C. by means of a suitable heat transfer medium such as superheated steam, hot air, molten salts, or some high temperature fluid. A uniform supply of heat is essential since the reaction proceeds with a calculated absorption of about 600 B.t.u. per pound of alcohol reacted, or 540 B.t.u. per pound charged with a 90% conversion as expected. The products of reaction with unchanged alcohol

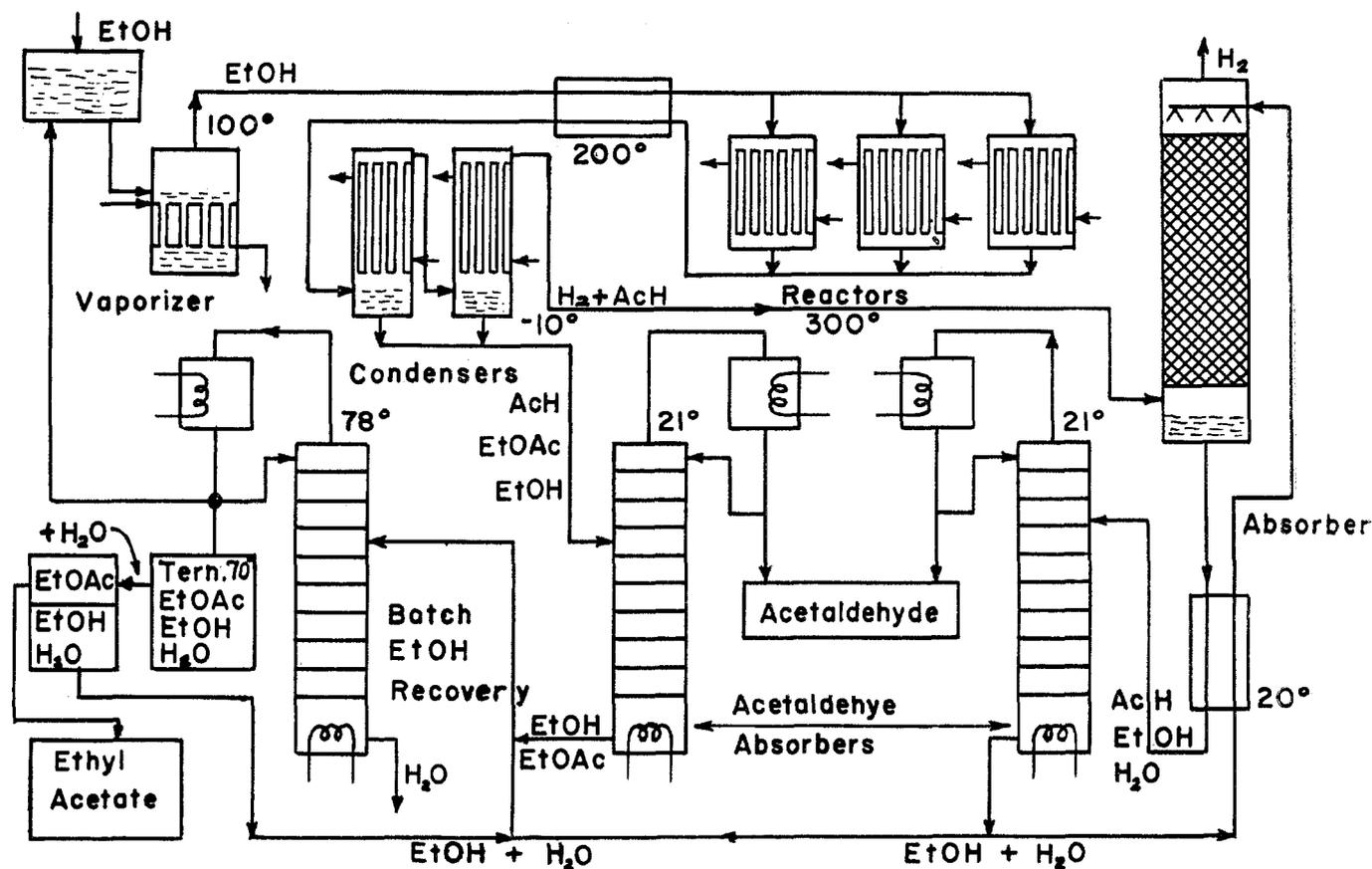


Figure 4. Proposed Dehydrogenation Process

are cooled after passage through the heat exchanger to  $-10^{\circ}\text{C}$ ., first with water and then with a refrigerant in two tubular condensers to condense as much of the alcohol, acetaldehyde, and ester as possible. The uncondensed gases are then sent to a dilute alcohol scrubber for removal of the remaining alcohol, acetaldehyde, and other dissolvable vapors. The hydrogen product collected from the scrubber may be used for hydrogenation purposes directly since it is about 98% pure containing only traces of unobjectionable by-products—methane, carbon monoxide, and ethylene. The alcohol-aldehyde condensate containing more than 90% of the reaction products is sent to a fractionating column for separation of the lower boiling acetaldehyde at  $21^{\circ}\text{C}$ .; the alcohol-ester bottoms are sent to a separate column for recovery of the alcohol at  $78^{\circ}\text{C}$ . Likewise the dilute alcohol scrubber solution is first fractionated in a column for recovery of the acetaldehyde product, the bottoms being sent to the alcohol recovery column. The ethyl acetate by-product, separated from the diluted ternary distillate of the alcohol recovery column, is purified in a separate column for recovery.

The dehydrogenation process is much simpler than the ethyl alcohol oxidation process for acetaldehyde. The temperatures of the dehydrogenation converters are only  $280^{\circ}\text{C}$ . as compared to a maximum temperature of  $550^{\circ}\text{C}$ . for the oxidation converters; hence fabrication and maintenance of this part of the equipment would be much easier. The endothermic nature of the dehydrogenation process makes it less imperative to maintain the desired operating temperature, but heating costs are higher. The exothermic reaction of the oxidation process, requiring heat removed for close control of the reaction temperature, is much more sensitive to loss in yield by fluctuations in temperature due to over-oxidation of the alcohol amounting to complete combustion and loss of starting material. Very small losses in yield and starting material occur with wide variations in temperature in the dehydrogenation method.

For continued uninterrupted operation of the dehydrogenation converter, where periodic reactivation of the catalyst is essential, several catalyst units are desirable so that reactivation of any of these can be made without serious curtailment of production. The reactivation can easily be made by shutting off the alcohol vapor feed to the converter, flushing with steam to remove alcohol vapor, passing hot air through the catalyst tubes while maintaining the temperature below  $400^{\circ}\text{C}$ . for about 1 hour, followed by alcohol reduction at  $280^{\circ}\text{C}$ . Careful control of the catalyst temperature during reactivation and the subsequent reduction are most essential, since both reactions are exothermic. Regulation of the amount and temperature of the air during the first stage is sufficient for maintaining the desired maximum temperature. During the reduction stage, which is perhaps more critical since a low temperature of reduction is desirable for a high activity and long life of the catalyst, the amount and temperature of the alcohol vapor can be regulated for a proper temperature control.

#### CONCLUSIONS

Various copper catalysts, supported and unsupported, some of which contained promoter materials, were thoroughly evaluated for their efficiency in the dehydrogenation of ethyl alcohol for the formation of acetaldehyde. These copper catalysts were prepared from the metal and several salts of copper, such as the carbonate, formate, hydroxide, nitrate, oxide, and cuprammonium complexes. The added promoter materials included cobalt metal and oxides of cobalt, chromium, magnesium, and zinc in varying amounts and in combinations. Supporter material consisted of alumina, alundum, pumice, and asbestos; various methods were used for impregnating these with the catalytic materials.

Under varying conditions of temperature and rate of passage of

the alcohol vapor, the maximum activity in terms of conversion of the alcohol to acetaldehyde and other valuable by-products, was determined. A majority of the catalysts were fairly specific; copper alone gave the highest yields of the aldehyde. A constant small amount of ethyl acetate was formed as the chief by-product with all the catalysts. For a sturdier type catalyst with fairly high activity, added cobalt and chromium as promoter agents were found beneficial; the former increased the percentage conversion of the alcohol and the latter contributed to a sustained high activity for a long continuous performance of the catalyst.

From a practical viewpoint, the best catalyst was the one prepared by impregnation of short-fibered asbestos with a solution of copper nitrate containing 5% cobalt oxide and 2% chromic oxide, based on the weight of copper oxide equivalent. At a temperature of 275° C. a maximum theoretical yield of 88% of acetaldehyde and 9.6% of ethyl acetate was obtained with a 93% conversion of the alcohol per pass. After 100 hours under these conditions the catalyst lost only 16% of its initial activity, and reactivation by a short air oxidation restored the activity to 105% of that initially present. Thus it was possible to obtain sustained activity, averaging 95% of the initial activity, over a long period by reactivations.

Based on the favorable results of this investigation, a potential process for the manufacture of acetaldehyde by the dehydrogenation of 95% ethyl alcohol is proposed.

## LITERATURE CITED

- (1) Anderson, J. W., Beyer, G. H., and Watson, K. M., *Natl. Petroleum News*, 36, R476 (1944).
- (2) Armstrong, E. F., and Hilditch, T. P., *Proc. Roy. Soc. (London)*, 97A, 259 (1920).
- (3) Assoc. Official Agricultural Chemists, "Tentative and Official Methods of Analysis," p. 195, 1945.
- (4) Baladin, A. A., *Z. physik. Chem.*, B2, 289 (1929); B3, 167 (1929).
- (5) Berthelot, M., *Les Carburés d'hydrogene*, 2, 202 (1901).
- (6) Constable, F. H., *J. Chem. Soc.*, 1578, 2795 (1927).
- (7) Davy, H., *Phil. Trans.*, 97, 45 (1817).
- (8) Dogolor, B. N., and Koton, M. M., *J. Gen. Chem. (U.S.S.R.)*, 6, 1444-51 (1935).
- (9) Dunbar, R. E., Cooper, D., and Cooper, R., *J. Am. Chem. Soc.*, 58, 1053 (1936).
- (10) Faith, W. L., and Keyes, D. B., *IND. ENG. CHEM.*, 23, 1250 (1931).
- (11) Faith, Keyes, and Clark, "Industrial Chemicals," New York, J. Wiley & Sons, 1950.
- (12) Grimax, E., *Bull. Soc. Chim. (II)*, 45, 481 (1886).
- (13) Groggins, P. H., "Unit Processes in Organic Synthesis," 3rd ed., p. 466, New York, McGraw-Hill Book Co., 1947.
- (14) Hightower, J. V., *Chem. & Met. Eng.*, 55, 7-105 (1948).
- (15) Ipatieff, V. N., *Ber.*, 34, 3579, 9596 (1901).
- (16) Johnson, J. Y., *Brit. Patent* 331,883 (1930).
- (17) Knoevenagel, E., and Heckel, W., *Ber.*, 36, 2816 (1903).
- (18) Kuhlman, F., *Ann.*, 29, 286 (1839).
- (19) Lorang, F. J. H., U. S. Patents 1,956,088 (1934) and 2,039,543 (1936).
- (20) Marchand, R. F., *J. Proct. Chem.*, 15, 7 (1838).
- (21) Neish, A. C., *Can. J. Research*, 23B, 49 (1945).
- (22) Orloff, J. E., "Oxidation des Alcohols par L'action de Contact," Paris (1901).
- (23) Palmer, W. G., *Proc. Roy. Soc. (London)*, 98A, 13 (1920); 99A, 412 (1921); 101A, 175 (1922).
- (24) Palmer, W. G., and Constable, F. H., *Ibid.*, 106A, 250; 107A, 255, 270 (1925).
- (25) Parks, G. S., and Huffman, H. M., "Free Energies of Some Organic Compounds," New York, Reinhold Pub. Corp., 1932.
- (26) Rideal, E. K., *Proc. Roy. Soc. (London)*, 99A, 153 (1921).
- (27) Sabatier, P., and Senderens, J. B., *Compt. rend.*, 136, 738, 921, 933 (1903).
- (28) Shreve, R. Norris, "Chemical Process Industries," 1st ed., p. 918, New York, McGraw-Hill Book Co., 1945.
- (29) Steverson, H., *Chem. Eng. News*, 27, 1182 (1949).
- (30) Strecker, A., *Ann.*, 93, 370 (1855).
- (31) Trillatt, A., *Bull. Soc. Chim. (III)*, 27, 96, 797 (1902).
- (32) U. S. Tariff Commission, Washington 25, D. C., "Production and Sales of Synthetic Organic Chemicals," 1948.
- (33) Whitmore, F. C., "Organic Chemistry," p. 243, New York, D. Van Nostrand Co., 1937.
- (34) Young, C. O., U. S. Patent 1,977,750 (1934).

RECEIVED September 15, 1950. In partial fulfillment of the requirements for the Ph.D. degree granted in June 1949. Contribution No. 19 from the Chemical Engineering Labs., Columbia University, New York, N. Y.

# Equilibrium Relations of Two Methane-Aromatic Binary Systems at 150° F.

M. ELBISHLAWI<sup>1</sup> AND J. R. SPENCER

Texas Petroleum Research Committee, University of Texas, Austin, Tex.

Previous work on mixtures of methane and hydrocarbons indicated a correlation between the chemical nature of the solvent and the solubility of the methane, the chemical nature being expressed by the Universal Oil Products characterization factor (13). The purpose of this work was to test the correlation for low values of the U.O.P. characterization factor and for systems containing aromatic hydrocarbons.

Equilibrium constants for the systems methane-benzene and methane-toluene which were studied bear out the correlation even to extreme ranges of the factors.

If, as these binary systems suggest, the solubility of methane in crude oil-natural gas systems has a similar dependence on the chemical character of the solvent, the prediction of phase behavior in petroleum reservoirs would be greatly facilitated. This prediction is of great economic importance in the petroleum industry, especially during the national emergency when oil and gas must be produced at maximum rates consistent without sacrifice of ultimate recovery.

BECAUSE of their importance in predicting the phase behavior of hydrocarbon systems, vapor equilibrium data for hydrocarbons have been extensively studied in the petroleum industry over the past two decades. Such data are usually used in the form of vaporization equilibrium constants as these can be applied directly to problems involving the effect of temperature and pressure on the compositions of liquid and vapor in two phase systems. This constant is defined as

$$k = \frac{y}{x} \quad (1)$$

where  $y$  is the mole fraction of the component in the vapor phase, and  $x$ , the mole fraction of the same component in the liquid phase.

Simplified systems of two and three components have been studied to provide a basis for the consideration of complex problems of more practical interest and thus enable the production

<sup>1</sup> Bureau of Mines, Cairo, Egypt.