Study on Fused Iron Catalyst for Alcohol Synthesis from Water-gas. IV. Reaction Rate and Composition of Product in the Synthesis with Catalyst Promoted by Copper

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Introduction

In a previous investigation¹⁾ with a small convertor a catalyst containing copper as a promoter gave a high yield of oxygenates from water-gas. However, the rate equation of reaction for the case was not derived, as the quantitative measurements of the rate at widely varying flow rates of synthesis gas were difficult.

The present investigation has been made to confirm the high yield of oxygenates with a synthesis under similar conditions of flow rate and temperature in a larger convertor of the same diameter and ten fold the previous catalyst content, and also to determine the equation of rate by means of a differential reactor procedure. The procedure had already been employed by R. B. Anderson et al²⁾ as well as H. Tramm³⁾ for the syntheses with a cobalt catalyst at normal pressure and an iron catalyst at high pressure respectively. According to their procedure the synthesis gas had been withdrawn from different heights of a catalyst bed during the synthesis to be analyzed for the reactants and products.

From the results obtained here, it appears that the synthesis product (solid and oil) contains a large amount of oxygenates, though slightly less than the previously reported yield, attaining to half the total yield, and that the reaction rate is similarly expressed by equations of two types for the rate controlled by the desorption of the adsorbed product and by the reaction on the surface respectively.

With respect to the lateral temperature gradient across the catalyst bed W. Broetz⁴⁾ made a brief description for the case of synthesis with an iron catalyst at high pressure. His differential equation of heat transfer has been analytically solved, with simplification and by combining with one of the rate equations obtained, to give the lateral temperature gradient of the catalyst bed.

Experimental Procedure

Apparatus.—The convertor was 16 mm. I. D. and 30 mm. O. D. by 3.5 m. high and cooled by an external oil (S. K. oil supplied by Yawata Iron Factory) circulation (refer to Fig. 1)*¹, and was packed with 620 cc. (1.4 kg.) of granules (1 to 2 mm. diameter) of the catalyst which had been exhaustively reduced at 500°C by hydrogen under normal pressure in a separate vessel. The catalyst contained the following promoters such as 3% Al_2O_3, 1% CaO, 1% MgO, 1% WO_3, 0.25%

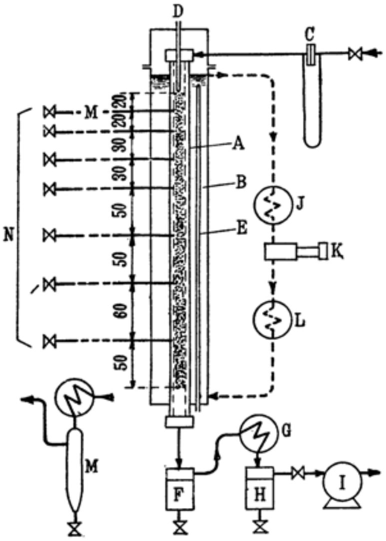

Fig. 1. Flow diagramm of synthesis.
A: Convertor B: Oil bath
C: Flow meter
D and E: Thermocouple well
F: Hot-separator G: Cooler
H: Cold-separator I: Gas meter
J: Coolor
K: Pump } for oil
L: Preheater
M: Water-cooler and separator
N: Sampling port

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1) H. Uchida, H. Ichinokawa et al., This Bulletin, 28, 68 (1955).

2) R. B. Anderson, A. Krieg et al., *Ind. Eng. Chem.*, 41, 2189 (1949).

3) H. Tramm, *Brennstoff Chem.*, 33, 21 (1952).

4) W. Broetz and W. Rottig, *Z. Elektrochem.*, 56, 896 (1952).

*¹ Since a pump capable of circulating hot oil was not available, the oil was cooled before entering the pump.

CuO, 0.5% K_2O in wt. % and gave a high yield of oxygenates in the small convertor as described previously. The catalyst bed was 3.1 m. high, and from successive seven ports at various intervals along the bed (refer to Fig. 1) quantities of gases, each not exceeding 7 vol. % of the entering gas, were alternatively led during the synthesis to a water-cooled separator, to be freed of oil and water. The gas from the exit of the convertor was also passed through a hot separator for removal of wax and then through a sequence of three cold separators for removal of oil. The gases, after the reduction of their pressure through respective reducing valves, were analysed for the reaction products, such as carbon dioxide, methane and gaseous olefin, as well as for the residual reactants, such as carbon monoxide and hydrogen. Their volumes were measured by gasmeters without removal of gasol and carbon dioxide.

The temperature was measured by a thermocouple placed in the catalyst bed near the entrance of convertor as well as by another inserted in the oil bath.

Synthesis.—The synthesis was conducted under a pressure of 25 kg./cm², at a flow rate of about 280 l./hr. (S. V., 450) of synthesis gas containing hydrogen and carbon monoxide in a ratio of 1;1, and at temperatures maintaining the synthesis at a desired apparent contraction[*2]. The steady state of synthesis was required for measurements and it was attained as follows: After an induction of 50 hr., during which the flow rate and the apparent contraction were kept considerably low (S. V., 250; the contraction less than 20%), the temperature was gradually raised until the contraction was about 45% at S. V. of 450; thereafter an additional operation of 30 hr. established tbe constant yield of solid plus liquid for a definite duration of synthesis. After the measurements at the contraction of about 45% (test No. 1) the temperature was adjusted to lower the contraction to about 35% (test No. 2) at the same S. V. for repeating series of measurements.

Composition of the Product.—The oily product was distilled into fractions of a temperature difference of 20°C under the atmospheric pressure and then a reduced pressure of 5 mmHg, until the final distillation temperature attained to 200°C and 190°C respectively. The fractions were then analyzed for alcohol, ester, cabonyl compound, olefin and paraffin[*3]. The aqueous product was first subjected to the determination of acid content, and then distilled into fractions for the determination of the content of alcohols (C_1—C_4). The products separated from the gases withdrawn through the ports were, however, too small in amount to be fractionated, and hence the average alcohol content in the aqueous products was estimated only as an equivalent of C_2-alcohol.

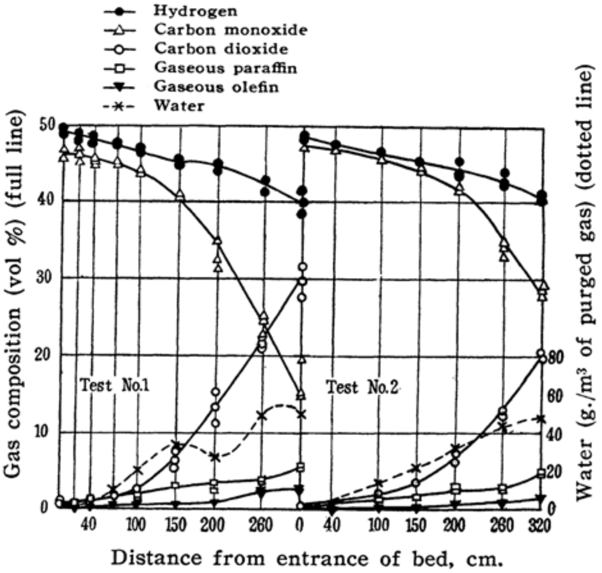

Fig. 2. Results of analyses for reactants and products in gases taken from bed and amounts of water obtained per m³. of purged gases.

[*2] The apparent contraction is defined as $1-E/F$, where E is the volume of exit gas containing gasol and CO_2, and F is the volume of feed gas at standard temperature and pressure.

[*3] The hydroxyl number, from which alcohol content in the fraction was estimated, was determined by acetylation at 100°C with acetic anhydride in pyridine. The saponification number was determined in the usual way with alcoholic potassium hydroxide. The carbonyl number was determined by reaction with hydroxylamine in alcoholic solution and titration with aqueous hydrochloric acid. Olefin contents were calculated from bromine number determined as usually (refer to H.L. Johnson et al., *Anal. Chem.*, 23, 869 (1951)), and paraffin contents were given as residues obtained by dissolving the fraction in a mixture of phosphoric anhydride and concentrated sulfuric acid (A.S.T.M. Standards (1953), Part 5, p. 1040).

Results and Computation

Results.—Results obtained from syntheses at apparent contractions of 46.3% and 36.1% are shown in Fig. 2 and Table I. In Fig. 2 the dotted curve indicates the amount, per 1 m^3 of purged gas, and of water given by the subtraction of amount of alcohol from that of aqueous product in the cold separator. The alcohol content tended to increase with the extent of conversion, as is shown in Table II. Table II shows use ratios of hydrogen to carbon monoxide for increasing conversion.

TABLE I

FLOW RATE AND CHARACTER OF EXIT GAS AND YIELD OF PRODUCTS

	Test No. 1	Test No. 2
Flow rate of entering gas g./h.	192	192
Flow rate of exit gas g./h.	151	162
Composition g./h.		
H_2	5	6
CO	27	62
CO_2	93	70
N_2	14	15
gaseous paraffin (CH_4)	6	5
gaseous olefin (C_3H_6)	6	4
Product obtained (aqueous)	7	9
in separator g./h. (oil+solid)	21	14
Difference between entering and exit gas g./h.	13	7
Use ratio (H_2 : CO)	1 : 1.25	1 : 1.34
(oil+wax+spirits)/m^3. (CO+H_2), g.	103	98
(C_3H_6)/m^3. (CO+H_2), g.	30	29
(CH_4)/m^3. (CO+H_2), g.	28	32

TABLE II

USE RATIO AND ALCOHOL CONTENT VARYING WITH LENGTH OF CATAŁYSET BED

	Distance from entrance, cm.							
	20	40	70	100	150	200	260	310
Use ratio Test No. 1	1.00	1.11	1.08	1.04	0.93	0.74	0.75	0.80
Test No. 2		1.80		1.10	1.04	0.92	0.81	0.75
Alcohol in ,, No. 1	0	1.6	2.4	3.3	4.7	3.3	8.2	10.5
aq. product ,, No. 2					3.0	4.6	4.0	12.1
(wt %)								

In the present experiment, as the method used for the analysis of the residual gases has been incapable of providing the details in composition of the gaseous hydrocarbon (C<5), the gaseous paraffin and olefin are roughly assumed to consist of methane and propylene respectively, as shown in Table I. This table shows that the flow rate of the entering gas differs slightly from that of the exit gas. The greater part of this difference might probably be due to the escape of lower alcohol and liquid hydrocarbon included by the purged gas through the separator.

The composition of the oil from test No. 1 is shown in Fig. 3. In this case the aqueous product amounted to about one third of the amount of oil plus solid, and contained 0.6% C_1-, 6%, C_2-, 1% C_3- and 3% C_4-alcohols with 2.4% acid equivalent in amount to acetic acid. The oil and aqueous product from test No. 2 contained a somewhat smaller amount of oxygenates than that from test No. 1, whereas the amount of aqueous product from test No. 2 was greater than from test No. 1. Though the amount of oxygenates produced in the larger convertor was slightly less than that in the previous small convertor, the catalyst produced invariably the oxygenates attaining to half the total yield even under the conditions less suitable for oxygenates formation than those in the Synol process.

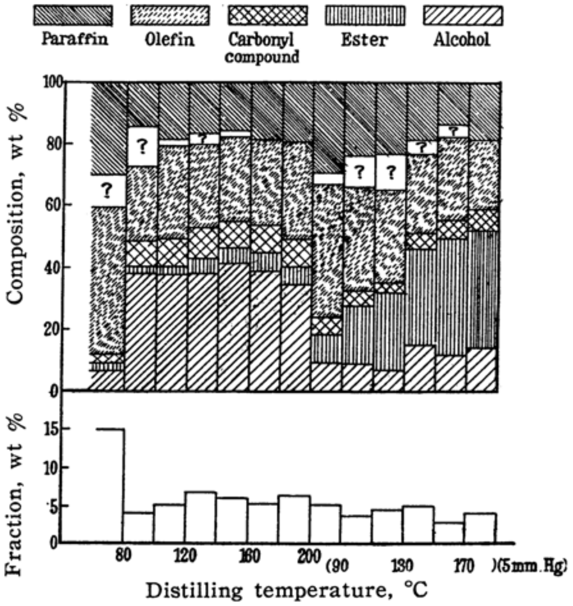

Fig. 3. Results of analyses for liquid product in test No. 1.

Computation of Partial Pressure of the Components in the Catalyst Bed.—The apparent contraction and the partial pressure of any component of synthesis gas entering the convertor at any point in the bed are computed from the results shown in Fig. 2.

Since the amount of oxygen appearing as oxygenates (but not water) in the separator of the exit attained to only a few per cent of the amount of oxygen supplied as carbon monoxide, the following oxygen balance is permissible.

$$Vf_{CO}=V'(f'_{CO}+2f'_{CO_2})+v_{H_2O}$$

where V is the volume of entering gas and V' the estimated volume of gases at different heights of the bed, both corresponding to normal temperature and pressure; f and f', the mole fractions referred to subscript in the entering gas and residual gas from the separator; v_{H_2O}, the volume of vapour at N.T.P. of the water obtained in the separator per V' of the residual gas. V' and hence the apparent contraction ($C=1-V'/V$) at any point in the bed may be evaluated from this oxygen balance in conjunction with the measured values of f, f' and v_{H_2O}.

TABLE III

COMPOSITION, FLOW RATE, AND PHYSICAL CHARACTERISTICS OF ENTERING AND EXIT GASES

	Entering gas		Exit gas	
	Test No. 1	Test No. 2	Test No. 1	Test No. 2
Composition				
H_2	49.3	48.0	36.0	37.6
CO	46.2	47.2	13.9	26.0
CO_2	0.4	0.5	29.3	18.6
N_2	4.1	4.3	6.9	6.2
H_2O			5.2	6.0
C_2H_6			5.3	3.9
C_6H_{12}			2.5	1.4
C_4H_9OH			0.7	0.3
Flow rate kg./h.	192	192	185	185
; l./h. at N.T.P.	283	277	174	196
C_p kcal./kg. °C	0.468	0.456	0.414	0.434
μ kg./m. h.	0.0851	0.0853	0.0813	0.0830
λ kcal./m. h. °C	0.1003	0.0990	0.0698	0.0765
C_pGS kcal./h. °C	0.0899	0.0876	0.0766	0.0803
U kcal./m². h. °C	58.1	57.7	51.5	52.5

The flow rate of gas and vapour in the convertor is, however, not directly related to V' because part of the oily product exists as a vapour. In this respect the amount of product from the hot separator predicted the amount of the liquid in the catalyst bed, since the separator was maintained at a temperature similar to that of the convertor. As for the mean molecular weight of the product (hydrocarbon and alcohol) in gaseous and vapour state at the exit the results in Fig. 3 and in Table I are available for the estimation when the fraction and composition of a product distilling below the lowest distillation temperature (140°C at 5 mmHg) of the total product in the hot separator are taken into account. The results are shown in Table III. Since the flow rates of the gases plus vapourized products at the exit of the convertor are available from the results in Table III, the flow rate and partial pressure of the components at any point of the bed are computed when the flow rate is assumed to vary proportionally with the change of V' (Fig. 4).

Consumption of Carbon Monoxide and its Rate.—The principal primary reaction of the synthesis with iron catalysts may be represented by the equation[*4]

$$\left.\begin{array}{c} H_2+CO\rightarrow-CHOH \\ -CHOH+H_2\rightarrow-CH_2-+H_2O \end{array}\right\} \qquad (1)$$

Alcohols or hydrocarbons may be formed as the results of the stepwise addition of methylene radicals to one end of a growing chain terminated by a hydroxymethylene radical or a methylene radical[5,6]. The water-gas shift-reaction (2) between carbon monoxide and water formed primarily by (1) may be the source of carbon dioxide[7,8]

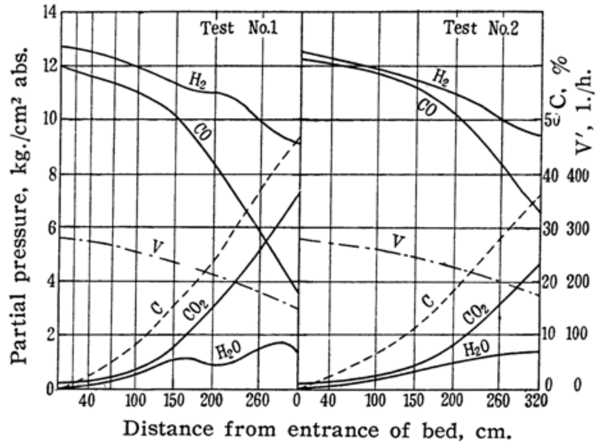

Fig. 4. Change of partial pressure of components, apparent contraction C, and volume of residual gas V′, with length of catalyst bed.

[*4] In the synthesis the reaction represented by the equation $H_2+2CO\rightarrow -CH_2- +CO_2$ would also take place. The previous investigation (*J. Chem. Soc. Japan*, (*Ind. Chem. Sect.*) **57**, 100 (1954)) revealed that the reaction took place actually in the synthesis with the catalyst containing silica as a promoter but not with the catalyst described in this paper.

5) E. J. Gibson and C. C. Gall, *J. Appl. Chem.*, **4**, 49 (1954).

6) A. W. Weitkamp and C. G. Fuge, *Ind. Eng. Chem.*, **45**, 363 (1953).

7) H. Koelbel and F. Engelhardt, *Chem. Ing. Tech.*, **22**, 27 (1950).

8) R. B. Anderson, B. Seligman et al., *Ind. Eng Chem.*, **44**, 391 (1952).

$$CO+H_2O\rightarrow H_2+CO_2 \tag{2}$$

The consumed amounts of carbon monoxide observed at different heights of the catalyst bed can be attributed to the sum of the amount of two kinds, the one from (1) and the other from (2), without conflict of evidence in the observed use ratios of hydrogen to carbon monoxide as well as the amount of water formed. When the evaluated amounts of carbon monoxide consumed according to either Eq. (1) or (2) are plotted against the quantity of the catalyst packed in the bed, Fig. 5 results. The curves in this figure may then be graphically differentiated to give the rates of the carbon monoxide consumption, cc. $CO_{conv.}$/hr. cc. catalyst.

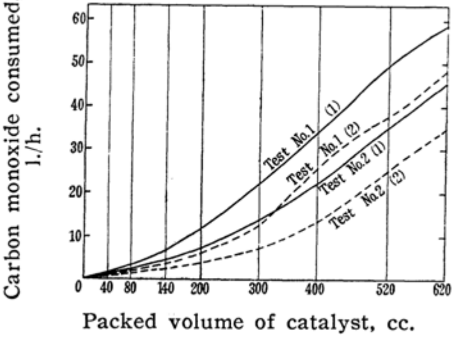

Fig. 5. Consumption of carbon monoxide by reaction (1) or (2) with increasing volume of catalyst.

Computation of Temperature Gradient in Catalyst Bed.—In the present experiment the temperature was measured in the oil bath along the wall of the convertor, but not in the catalyst bed except at the top. The temperature gradient thus measured might relate to the longitudinal distribution in the bed by the usual computation as follows.

Although S. Kodame et al.[9] already pointed out that the true temperature gradient in the catalyst bed where the heat of reaction was great and simultaneously the flow rate was small could not be given unless a three dimensional mathematical treatment of the problem should be employed, the treatment was so difficult in this case, where no rate equation had yet been given, that the calculation was conducted conventionally under the assumption of uniform temperature in the lateral direction of the bed. Under this assumption the rise of temperature due to the heat of synthesis in the longitudinal direction of the bed might be usually given by Eq. (3) or (4).

$$C_pGS\frac{dt}{dx}=S\sum_i\phi_i q_i-2\pi RU(t-t_w) \tag{3}$$

$$C_pGS\Delta t=Q-2\pi RU\Delta x(t-t_w) \tag{4}$$

In Eqs. (3) and (4), C_p is specific heat at a constant pressure, kcal./kg. °C; G, mass velocity of the fluid kg./m² hr.; S, cross sectional area of the convertor, m²; x, height of the bed from the top, m; t, mean temperature of the bed at x from the top, °C; t_w, temperature measured in the oil, °C; ϕ_i, rate of ith reaction, cc. CO/hr. cc. catalyst; q_i, heat of ith reaction, kcal./cc. CO; U, overall coefficient of heat transfer kcal./m². hr. °C; R, radius of the bed, m; and Q is heat evolved by reaction in a volume $S\Delta x$, kcal./hr. The values of C_pGS and U at the entrance and the end of the bed are computed to give the results as shown in Table III[*5]. C_pGS and U are expressed as functions of the bed length as shown in Fig. 6, when they are again assumed to vary proportionally with the change of V'.

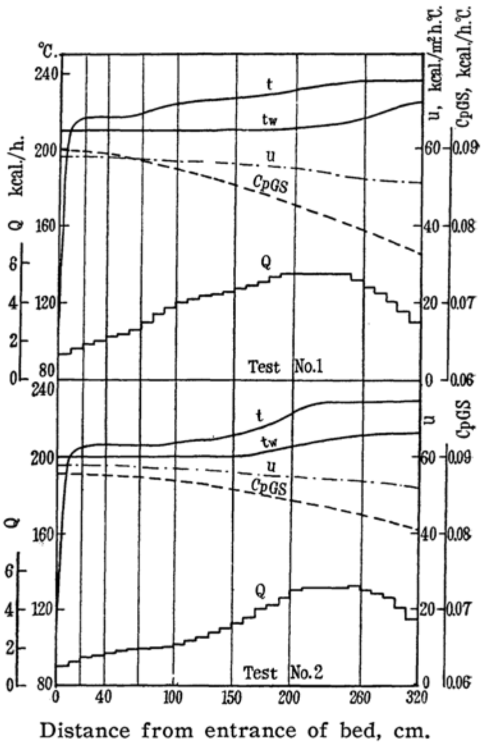

Fig. 6. Temperature measured in oil bath (t_w), C_pGS, and heat of synthesis (Q) related to bed length, and temperature gradient in bed.

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9) S. Kodama and K. Fukui, *Kagaku Kikai* (*Chem. Eng.*), **12**, 72 (1948) (in Japanese).

[*5] The computations were conducted as follows: The values of C_p were obtained from the additive property with the corrections upon pressure by Hougen-Watson of the components. The viscosity and the thermal conductivity were evaluated by the application of the Wilke's method (*J. Chem Phys.*, **18**, 517 (1950)) and the Lindsay-Bromley's (*Ind. Eng. Chem.*, **42**, 1508 (1950)) respectively, with which the theorem of corresponding state being used. The values obtained are listed in Table III. The heat transfer coefficient between S.K. oil and the wall of the convertor was computed by means of the equation in annular spaces for the case of laminar flow by C.Y. Chen et al (*Trans. A.S.M.E.*, **68**, 99 (1946)), and attained to the value of 44.4 kcal./m²hr.°C. The heat transfer coefficient based upon the average temperature of the packed bed for the entering and exit gases was computed by use of the equation by S. Hatta et al. (*Kagaku Kikai*, **12**, 58 (1948); **13**, 79 (1949) (in Japanese)) which was applicable to the present experiment (R_e<100) and resulted in a respective value of 198 and 136 kcal./m²hr.°C, from which the respective overall heat transfer coefficient was consequently given (Table III).

The heat evolved in the synthesis is also expressed as a function of the bed length, as shown in Fig. 6, from the amount of carbon monoxide consumed according to either (1) or (2), by employing 620 kcal./m³ (H_2+CO) and 9.0 kcal./mol. CO for the heats of reaction by (1) and (2) respectively. From these distributions together with the temperature gradient in the oil bath the temperature is expressed as a function of the bed length when a numerical stepwise computation by trial and error method is employed for Eq. (4) by starting the process from a bed length of 10 cm. from the entrance.

Discussion

Rate Equation of the Synthesis.—Data available for kinetic interpretation are generally obtained from the measurement in an isothermic convertor with a small amount of catalyst, however, in the synthesis such as described in this paper the yield in products such as oil and water is usually too small to permit a detailed treatment of the rate. Although the present experiment was conducted in the convertor with a temperature gradient in the bed, the results were available for the interpretation, as two portions nearly isothermic over a relatively wide range of the catalyst bed were fortunately present.

Rate equations for the synthesis, based on different steps as the rate determining step in terms of the Hougen-Watson's classification, are listed in Table IV together with the equations once proposed by R. B. Anderson et al[10] and H. Tramm[3]. The equation (h) by the former was based on the desorption of adsorbed product as the rate determining step, while that by the latter was not obvious about the rate-determining step in terms of the above classification. S. Kodama[11] proposed the rate equation given by $\phi=d[CH_2]/dt=kC_{\text{carbide}}C_{\text{H}}^2$, where C_{H} is the concentration of hydrogen adsorbed with dissociation no the catalyst surface. The equation resulted in Eq. (c) when C_{carbide} could be assumed equivalent to CO_{ad}, however, the mechanism seemed somewhat improbable[12]. With respect to the components adsorbed on the surface, only one component among the reactants and products was taken into consideration, since the two components made the equation too complicated to be used for the interpretation of the experimental results, whereas an equation without consideration of the adsorbed component, such as Eq. (f) by R. B. Anderson et al for the synthesis with an iron catalyst, proved too simplified to permit the interpretation.

The Equations may be generalized to Eq. (5) which is then rearranged to Eq. (6)

$$\phi=k\overset{i}{\Pi}p_i/(1+k'\overset{j}{\Pi}p_j)^n \tag{5}$$

$$\sqrt[n]{\overset{i}{\Pi}p_i/\phi}=\sqrt[n]{1/k}+\sqrt[n]{k'^n/k}\,\overset{j}{\Pi}p_j \tag{6}$$

The correct assumption gives a straight line with a positive value of slope and intercept when values of $\sqrt[n]{\overset{i}{\Pi}p_i/\phi}$ are plotted against $\overset{i}{\Pi}p_i$. In Fig. 7, some of the rate equations are shown, being thus plotted, and the Eq. (a), (b), and (h) appear to be more adequate expressions of the rate. The values of k and k' at the temperatures of 229 and 237°C are hence computable and then the apparent activation energy is obtained by the Arrhenius' equation to give the values shown in Table V. From these values here obtained, the rates of synthesis at different temperatures are computed by the respective equations and compared, as shown in Table VI,

TABLE IV
RATE EQUATION

Surface reaction controlling		
$CO_{\text{ad}}+H_{\text{ad}}\longrightarrow COH_{\text{ad}}$	$\phi=kp_{H_2}{}^{1/2}p_{CO}/(1+k'p_{CO})^2$	(a)
$COH_{\text{ad}}+H_{\text{ad}}\longrightarrow CHOH_{\text{ad}}$	$\phi=kp_{H_2}p_{CO}/(1+k'p_{CO})^2$	(b)
$CO_{\text{ad}}+2H_{\text{ad}}\longrightarrow CHOH_{\text{ad}}$	$\phi=kp_{H_2}p_{CO}/(1+k'p_{CO})^3$	(c)
Adsorption controlling		
$H_2\longrightarrow 2H_{\text{ad}}$	$\phi=kp_{H_2}{}^{1/2}/(1+k'p_{CO})$	(d)
$CO\longrightarrow CO_{\text{ad}}$	$\phi=kp_{CO}/(1+k'p_{H_2}{}^{1/2})$	(e)
By Anderson (Fe-catalyst)	$\phi=kp_{H_2}$	(f)
Desorption controlling		
$\text{Product}_{\text{ad}}\longrightarrow\text{Product}$	$\phi=(kk'p_{H_2}{}^2p_{CO}/p_{H_2O})/(1+k'p_{H_2}{}^2p_{CO}/p_{H_2O})$	(g)
By Anderson (Co-catalyst)	$\phi=kk'p_{H_2}{}^2p_{CO}/(1+k'p_{H^2}{}^2p_{CO})$	(h)
By Tramm	$\phi=(kp_{H_2}{}^2/p_{CO})/[1+k'(p_{CO_2}+p_{H_2O})^5]$	(i)

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[10] H.H. Storch, N. Golumbic et al, "Fischer-Tropsch and Related Syntheses", (1951), pp. 529, 554.

[11] S. Kodama, *J. Chem. Soc. Japan*, 62, 1185 (1941) (in Japanese).

[12] O. A. Hougen and K. M. Watson, "Chemical Process Principles", (1950), p. 924.

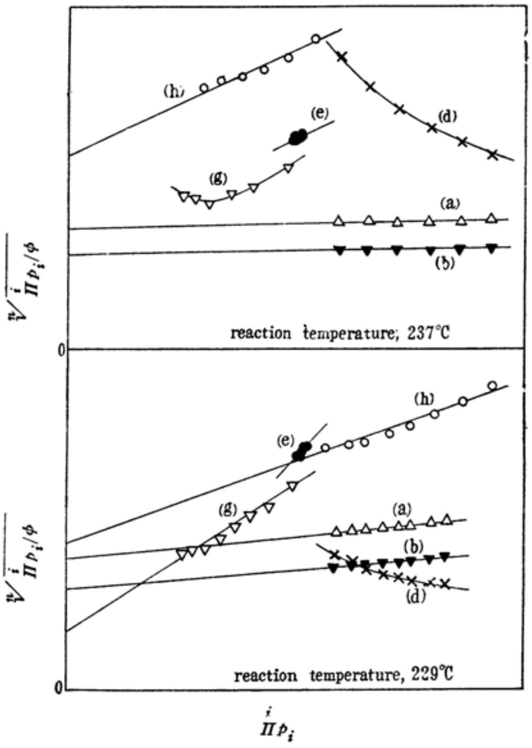

Fig. 7. Experimental rate plotted by various rate equations in Table IV.

with the experimental rate obtained from Fig. 5. Table VI shows good agreement with three rate equations and the agreement is incontestable among them.

With respect to the water-gas shift reaction accompanying the reaction (1), the following rate equation by Padovani-Lotteri[13] is employed

$$\phi=k(p_{H_2O}p_{CO}-Kp_{H_2}p_{CO_2}) \tag{7}$$

and the rate constant as well as the apparent activation energy is similarly evaluated to give the values of 13.45, 9.14 cc. CO/cc. Cat. hr. atm² for the former in test No. 1 and No. 2 respectively, and 24.5 kcal./M for the latter. The agreement between the rates computed from the values thus obtained and the experimental is, however, less satisfactory than that attained in the reaction (1).

Lateral Temperature-distribution of Catalyst Bed.—W. Broetz et al[4] gave a following differential equation (Eq. (8)) of lateral heat transfer across the catalyst bed, provided that the temperature were uniform in the direction of gas flow and, at the same time, the concentrations uniform across the bed

$$d^2\theta/dr^2+(1/r)(d\theta/dr)+\sum_i \dot{n}_{iw}Q_i e^{B_i\theta}/\lambda=0 \tag{8}$$

In the equation, r is a lateral distance from center, m; θ, temperature difference between

TABLE V

VALUES OF k, k', AND APPARENT ACTIVATION ENERGY OBTAINED FROM Eqs. (h), (b) and (a)

Equation	Temperature °C	k		k'		Energy of activation
	237	347		0.918×10^{-3}		
Eq. (h)			cc. CO/cc. cat. hr.		atm^{-3}	22.3
	229	244		0.902×10^{-3}		
	237	2.81		2.58×10^{-2}		
Eq. (b)			cc. CO/cc. cat. hr. atm^2		atm^{-1}	25.8
	229	1.88		2.70×10^{-2}		
	237	2.88		1.23×10^{-2}		
Eq. (a)			cc. CO/cc. cat. hr. $atm^{1.5}$		atm^{-1}	25.9
	229	1.91		1.27×10^{-2}		

TABLE VI

COMPARISON OF EXPERIMENTAL RATE WITH RATES COMPUTED FROM Eqs. (h), (b) and (a)

Temperature °C	Test No.	Distance from Entrance cm.	Rate obtained from Fig. 5 cc. CO/h. cc. cat.	Rate computed from		
				Eq. (h)	Eq. (b)	Eq. (a)
237	1	260	119	119.8	122.3	119.2
	1	300	85	85.0	88.2	85.2
229	2	250	109	110.5	110.2	113.0
	2	290	96	92.6	93.1	94.2
222	1	90	105	109.9	102.9	103.2
	2	198	99	98.0	88.6	90.3
217	1	30	63	85.5	81.9	82.1
207	2	90	50	51.8	44.2	45.6

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[13] C. Padovani and A. Lotteri, *J. Soc. Chem. Ind.*, 56, 391T (1937).

catalyst bed and oil bath, °C; $\dot{n}_{iw}$, rate of ith reaction corresponding to the temperature of oil bath, mol. CO/m³ cat.; Q_i, heat evolved by ith reaction, kcal./mol. CO; λ, effective thermal conductivity of packed bed, kcal./m. hr. °C; B_i is given by $B_i=E_i/\mathbb{R}T_w^2$[*6], where E_i is apparent activation energy of ith reaction, T_w, temperature of oil bath, °K; $\mathbb{R}$, gas constant. On the basis of this equation, he derived a relation between $\dot{n}_{iw}$ and $\bar{\dot{n}}_i$, the rate averaged over a cross section in the bed. In the derivation, he gave graphically or numerically the lateral temperature distribution as a function of $R\sqrt{\dfrac{B\bar{\dot{n}}_iQ_i}{\lambda}}$, but not analytically[14].

Attempts are made here of an analytical solution with simplification of the Broetz's equation and also of its application to the experimental results. The boundary conditions for Eq. (8) are given by

$$-\lambda(d\theta/dr)=U'\theta \quad \text{at } r=R$$

and θ has a finite value at $r=0$

U' is overall heat transfer coefficient, kcal./m² hr. °C, and R, radius of the bed. The equation can neither be analytically solved nor numerically integrated without tedious computation, but reduces to an equation similar to that obtained by R.H. Wilhelm et al[15]. when the terms higher than the third in the expanded series of $e^{B\theta}$ are neglected, and then it is solved to give Eq. (9)

$$\left.\begin{aligned}
&\theta=\frac{C}{A}\left[\frac{J_0(r\sqrt{A})}{D}-1\right]\\
&A\equiv\sum_i \dot{n}_{iw}Q_iB_i/\lambda, \qquad C\equiv\sum_i \dot{n}_{iw}Q_i/\lambda\\
&D\equiv U'J_0(R\sqrt{A})-\lambda\sqrt{A}J_1(R\sqrt{A})
\end{aligned}\right\} \tag{9}$$

where J_0, J_1 are the Bessel functions of first kind, zeroth and first order respectively. From the equation in conjunction with the observed data, such as the composition of gaseous product, t_w (temperature of oil bath, °C) and the rate equation, the temperature difference θ in the portions of convertor with relatively uniform temperature in the direction of gas flow is given as a function of lateral distance r in Fig. 8. In the computation, B_i is evaluated from the observed t_w and the apparent activation energy (25.8 and 24.5 kcal./mol. for the reaction (1) and (2) respectively), and also $\dot{n}_{iw}$ from the rate equation (h) (Table IV) and Eq. (7) employing the values of k, k' and the partial pressures in gaseous product and hence A and C are consequently determined. D is computable from the values of U' (83.5 and 81.4 kcal./m². hr. °C. at points 90 and 260 cm. apart from the entrance respectively) and λ (0.636 and 0.443 kcal./m. hr. °C.) which are similarly obtained as previously described.

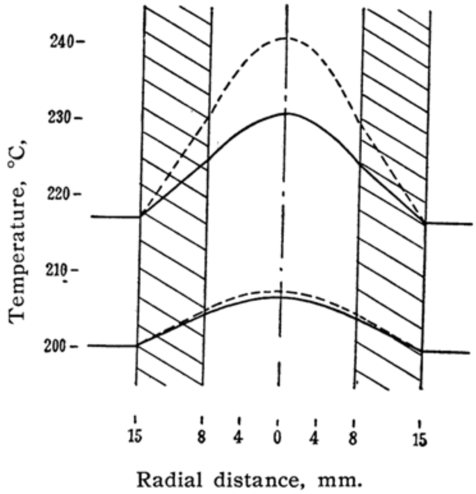

Fig. 8. Lateral temperature gradient in bed computed by Eq. (8). above; Test No. 1, 260 cm. apart from entrance. below; Test No. 2, 90 cm. apart from entrance. full line, analytical solution with simplification. dotted line, numerical computation.

In this figure, it appears that the higher terms may no longer be ignored when θ is larger than 10°C. This is conceivable from the value of B of about 0.05 and illustrated in the temperature-diameter curve at the point 260 cm. apart from the entrance.

Summary

The catalyst containing copper as a promoter has produced a good yield of the oxygenates in the small convertor (volume of the catalyst, 60 cc.) as well as in the larger convertor (620 cc.). Although the syntheses have been conducted at relatively low space velocity of the synthesis gas as compared with the Synol synthesis, the oxygenates amount to so high a value as half the liquid

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[*6] W. Broetz introduced a relation between the reaction rate ($\dot{n}_i$) at T°K in the catalyst bed and the one ($\dot{n}_{iw}$) corresponding to the temperature in the oil bath, which was given by

$$\dot{n}_i=\dot{n}_{iw}\cdot\exp^{-\frac{E_i}{\mathbb{R}\cdot T\cdot T_w}(T_w-T)}$$

He assumed the following relation when T differed not so much from Tw

$$E_i/\mathbb{R}\cdot T\cdot T_w=E_i/\mathbb{R}\cdot Tw^2=B_i,$$

and attained to

$$\dot{n}_i=\dot{n}_{iw}e^{B_i\theta}.$$

14) W. Broetz, *Z. Elektrochem.*, 57, 470 (1953).

15) R. H. Wilhelm, W. C. Johnson et al., *Ind. Eng. Chem.*, 35, 582 (1943).

and solid products and the result may promise the higher yield of oxygenates at the working conditions analogous to those with the Synol synthesis.

From the results of analyses for the reactants and products in the gases withdrawn from seven different heights of the catalyst bed together with the results of the composition of the product at the exit and also with special attention paid to the temperature gradient and flow rate through the catalyst bed, two types of the rate equation have been presented as shown by Eq. (A) and Eq. (B), both of which are similarly applicable to the observed rate.

$$\phi = kk'p_{H_2}^2 p_{CO}/(1+k'p_{H_2}^2 p_{CO}) \qquad (A)$$

$$\phi = kp_{H_2}p_{CO}/(1+k'p_{CO})^2,$$

$$\phi = kp_{H_2}^{1/2} p_{CO}/(1+k'p_{CO})^2 \qquad (B)$$

The equation (A) was once proposed by R. B. Anderson et al. for the synthesis with a cobalt catalyst.

The lateral temperature distribution in the catalyst bed is given by a simplified analytical solution of the W. Broetz's equation of the heat transfer only when the temperature difference between the wall of the convertor and the catalyst bed is considerably small.

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