Concentration and Temperature Profiles in a Tubular Reactor for Methanol Synthesis with an Outer-wall of Uniform Temperature. I. Profiles in a Reactor without a Heat Exchanger in a Catalyst Bed

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The heat transfer problem concerning methanol synthesis reactor placed in a bath of boiling heat transfer medium has been discussed in a paper by Wirth¹⁾, but his paper deals with neither the concentration profile nor the temperature profile in the catalyst bed. The present paper provides sets of concentration and temperature profiles obtained by the use of a tubular reactor for the methanol synthesis. The reactor was placed in a bath of flowing hot oil, and the determination of the profiles was conducted in essentially the same way as that used with the Fischer-Tropsch synthesis reactors in this laboratory²,³⁾. Starting with the experimental concentration profile, calculation of the axial temperature profile by means of the conventional procedure was attempted in order to find out the reasonable values of heat transfer coefficients by comparison of the resultant profile with the experimental profile. In view of the most favorable temperature profile for methanol production, the experimental profile, in conjunction with the heat transfer efficiencies thus obtained, may be helpful in predicting a suitable means for improving the reactor performance.

Experimental

The synthesis gas, consisting of three parts hydrogen and one part carbon monoxide plus a small amount of inert gas (5~7% nitrogen), was furnished in a gas holder (400 m³) by adding an amount of electrolytic hydrogen to water-gas produced in a water-gas generator. Before this addition, the water-gas was passed through a gas purification train in a method described elsewhere¹⁾, and the sulfur content was reduced to about 1 p.p.m. Figure 1 shows a schematic diagram of the methanol synthesis. The synthesis gas was compressed by a gas compressor (A) to 250 kg./cm² and was then introduced into a high pressure gas storage (B), from which the compressed gas was injected as a make-up gas into a synthesis loop through a reducing valve (V_1). The synthesis loop consisted of a gas purifier (D) filled with active charcoal, a preheater (E) for the synthesis gas, a reactor (F), a cooler (G), two methanol separators (H_1 and H_2), a gas circulating pump (I), and an oil separator (J) for removal of oil from the pump. Injection of the make-up gas was made immediately before the purifier in the synthesis loop in order that the gas might be removed from the last traces of sulfur prior to its entering the reactor. Part of the circulating gas was always being purged from the loop through a reducting valve (V_2) to keep the inert gas content below a certain limit, and the flow rate of purged gas was determined by means of a gas meter at atmospheric pressure. Moreover, the compressor was connected in order to allow compression of hydrogen into the synthesis loop through a reducing valve (V_3). The flow rates of the make-up gas and the circulating gas were determined by means of high pressure flow meters, C_1 and C_2 respectively.

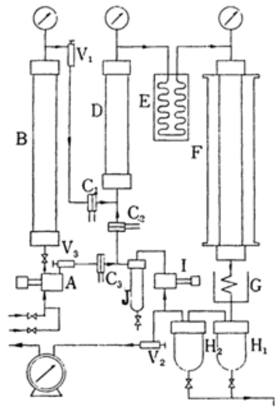

Fig. 1. Schematic diagram of methanol synthesis.

A detailed sketch of the reactor is given in Fig. 2. The reactor had a total length of 2 m., an outer diameter of 100 mm., and an inner diameter of 50 mm., and was made of chromium steel (13% Cr). It was placed coaxially in a cylinder 300 mm. in diameter. Into the bottom of the cylinder, a heat tranfer medium (Kanechlol) was fed at a flow rate of 1.2 m³/hr.; it passed upwards through an annular space between the reactor and the cylinder wall to the top, where the medium was allowed to flow down into a reservoir maintained at a fixed high temperature. The catalyst charge was 1.74 l. with a layer of 1 l. copper granules placed above the catalyst bed. The catalyst bed was 950 mm. high, occupying the intermediate range of the

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1) G. Wirth, *Chem. Tech.*, **5**, 253 (1953).

2) M. Kuraishi, H. Ichinokawa, K. Ogawa, K. Kurita, T. Hosoya and H. Uchida, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1588 (1960).

3) M. Kuraishi, M. Kurita, T. Hosoya, H. Ichinokawa, K. Ogawa and H. Uchida, This Bulletin, **34**, 780, 1101 (1961).

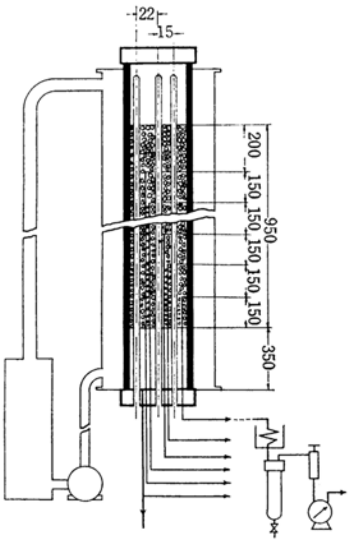

Fig. 2. Methanol synthesis reactor.

reactor between 350 and 1300 mm. from the bottom. Three thermocouple protection tubes of stainless steel went through the whole length of the catalyst bed. One of the tubes was a center thermocouple tube 8 mm. in outer diameter and with a thickness of 2 mm., while the others were off-center thermocouple tubes 5 mm. in outer diameter with a thickness of 1 mm. and were arranged in such a manner that they went through the bed 13 mm. and 22 mm. apart from the center axis respectively. The thermocouples could be moved upwards and downwards to permit scanning of the axial temperature profiles along the protection tubes.

Five small copper tubes, 2 mm. in outer diameter and 0.5 mm. thick, of different lengths were placed parallel in the catalyst bed, and from five successive ports, at 150, 300, 450, 600 and 750 mm. above the bottom of the bed, small portions of the fluid in the catalyst bed were withdrawn at a flow rate of 30 l./hr. out of the reactor; they then passed separately through small coolers and separators (50 cc. in volume) in order to produce the liquid product. Moreover, a small portion was led in the same way from the outlet tube by way of a tee placed immediately after the reactor. The gaseous product was reduced to atmospheric pressure, metered and analyzed, while the liquid product obtained in the small separators was weighed and analyzed. The analyses were made by means of gas chromatography as well as by conventional chemical methods. From the results of the analyses and the amounts of methanol obtained in the separators, the composition of the fluids at the five ports in the catalyst bed, as well as that of the exit gas, could be calculated.

For satisfactory performance of the reactor, caution had to be exercised, particularly at the beginning of the synthesis, to avoid a sudden temperature rise in the catalyst bed, which would cause an ignition of the catalyst granules. The entire system, accordingly, was first charged with hydrogen, which was circulated at about 100 kg./cm^2, while the heat transfer medium was heated up to 295°C. The make-up gas was then gradually introduced until the total pressure reached 200 kg./cm^2. The carbon monoxide content was subsequently increased by discharging continuously part of the circulating gas and by charging, in turn, the make-up gas until the synthesis could allow the collection of reliable performance data.

A three-component catalyst consisting of oxides of zinc, chromium and copper was used in this synthesis. Prepared in the way described previously4), it contained zinc, chromium and copper in the atom ratios of $Cr/Zn=0.49$ and $Cu/Zn=0.16$. Before use in the synthesis, the catalyst was reduced in a separate oven at about 240°C in a current of the synthesis gas at atmospheric pressure. The catalyst granules were 3 mm. in diameter by 4 mm. high, and 1.74 l. of the reduced granules weighed 2.43 kg.

Results

Methanol Yield.—The methanol yields are illustrated in Table I, together with the corresponding operation variables. The yield, expressed by the space-time yield of the reactor, is rather lower than is usual with commercial reactors. It becomes higher as either the flow rate of the inlet gas is increased or as the

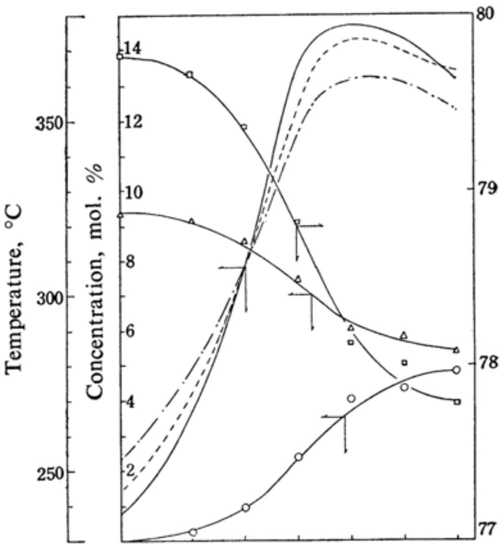

Fig. 3. Axial concentration and temperature profiles. Exp. 1.

Temperature profiles
—— Center profile
------ Off-center profile at r=15 mm.
—·— Off-center profile at r=22 mm.
Concentration profiles
—○— Methanol
—△— Carbon monoxide
—□— Hydrogen

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4) Y. Ogino, M. Oba and H. Uchida, ibid., 33, 358 (1960).

TABLE I. OPERATION VARIABLES AND METHANOL YIELD

Exp.	Flow rate of inlet gas	Composition of inlet gas[a]	Oil bath temperature	Bed temperature		Methanol yield	Space-time-yield
				top	bottom		
	l./hr.	H_2/CO	°C	°C	°C	kg./day	kg./l. hr.
1	33570	8.5(10.9)	295±1	246	359	50.6	1.21
2	30000	8.6(10.8)	295±1	245	362	50.4	1.21
3	34600	9.1(10.1)	295±1	235	359	48.9	1.17
4	38740	8.0(9.2)	295±1	243	364	60.3	1.44
5	31070	9.1(9.8)	295±1	256	356	47.2	1.13
6	24680	9.7(10.0)	295±1	243	359	41.2	0.99
7	19430	10.7(9.5)	295±1	256	328	35.1	0.84
8	19980	10.5(10.4)	295±1	255	332	33.1	0.79
9	41130	4.8(6.9)	295±1	232	385	56.0	1.34
10	34470	3.0(7.7)	295±1	239	374	42.2	1.01

[a] Numerals in bracket indicate the inert gas content (vol. %).

ratio of hydrogen to carbon monoxide is decreased. The synthesis product contains only 1~3% water and 0~0.3% methyl formate as its impurities. Very little carbon dioxide or methane was detected in the exit gas from the reactor.

Temperature and Concentration Profiles in Catalyst Bed.—As is shown by the examples in Figs. 3 and 4, the axial profiles differ in minor details, even though the flow rate of the inlet gas and the composition of the synthesis gas vary within a certain range. The bed temperature remains below the oil bath temperature in the top zone of the catalyst bed, it rises rapidly in the intermediate zone, and, after having its maximum value, it decreases slowly in the bottom zone. In contrast to this, the methanol concentration is extremely low in the top zone, begins to rise in the intermediate zone, and continues to rise more slowly until the equilibrium concentration is attained at the bottom of the bed.

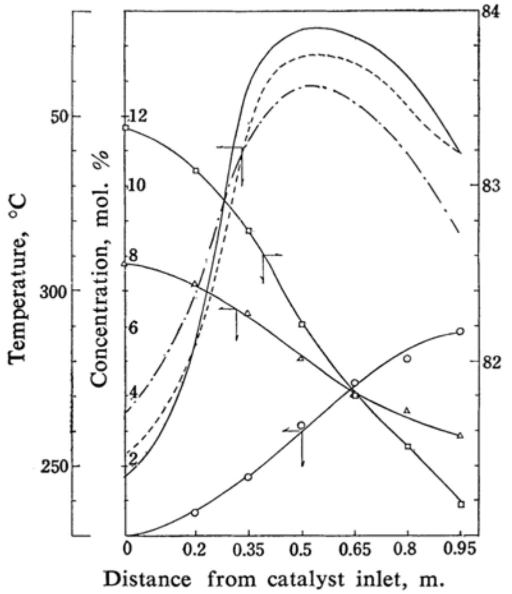

Fig. 4. Axial concentration and temperature profiles. Exp. 7.

Temperature profiles
—— Center profile
------ Off-center profile at r=15 mm.
—·— Off-center profile at r=22 mm.
Concentration profiles
—○— Methanol
—△— Carbon monoxide
—□— Hydrogen

As is shown in Fig. 5, the radial temperature profile is concave upwards at the top of the bed, becomes flat in the intermediate zone, and finally turns convex upwards at the lower zone. The temperature rise over a cross section of the catalyst bed reaches as high as about 40°C in the bottom zone. Within the present

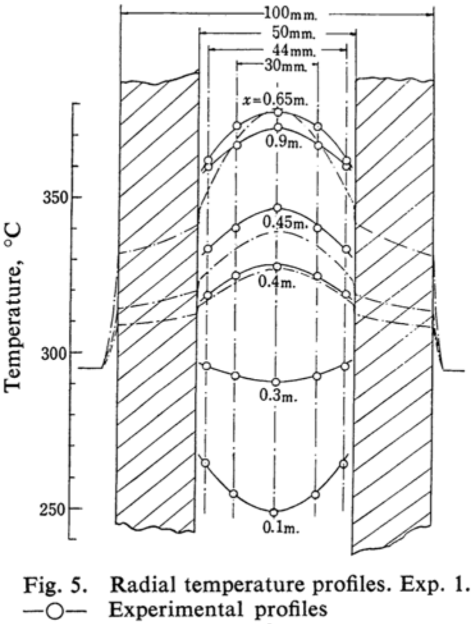

Fig. 5. Radial temperature profiles. Exp. 1.
—○— Experimental profiles
—·— Calculated profiles

range of operation conditions, the magnitude of the temperature rise increases with a decreasing ratio of hydrogen to carbon monoxide.

Axial Distribution of Reaction Heat.—The combination of the concentration data along the bed with the methanol yield of the reactor, as well as with the flow rate of the inlet gas, leads to the methanol flow rate as a function of the bed length (cf. the solid-line curve in Fig. 6). When the whole bed length is divided into six steps according to the heights of the ports at which a small portion of the fluid is withdrawn, the methanol yield within each step can be readily obtained from the flow rate curve (cf. the step-by-step dotted-line plot). Multiplication of the methanol yield by Thomas'5) thermochemical data on the reaction heat of the methanol synthesis results in a step-by-step plot of the reaction heat (cf. the dotted and dashed-line plot). In the multiplication, the reaction heat is assumed to take a value corresponding to the temperature averaged throughout each step on the basis of the average temperature over a cross section.

Catalyst Activity.—The activities for the methanol synthesis of the catalyst samples before and after the present synthesis have been determined by the use of a small separate reactor (catalyst bed, 10 cc.), as has been reported previously6). The operating variables were as follows: the pressure was 150 kg./cm^2, the space velocity was 1×10^4 hr^{-1}, and the H_2/CO ratio was 2. The results are shown in Fig. 7. Although the activity is high immediately after the reduction of the raw catalyst at 250°C (plot A), it becomes lower as the catalyst undergoes heating at higher temperatures, as is shown by plots B and C, obtained with the catalyst samples after heating them at 360 and 450°C for two hours respectively. The activity of the catalyst sample after the synthesis runs (plot D) 1—10 lies even lower than plot C. This low activity is probably due to the poisoning effect of sulfur, a minute amount of which is perhaps contained in the inlet gas.

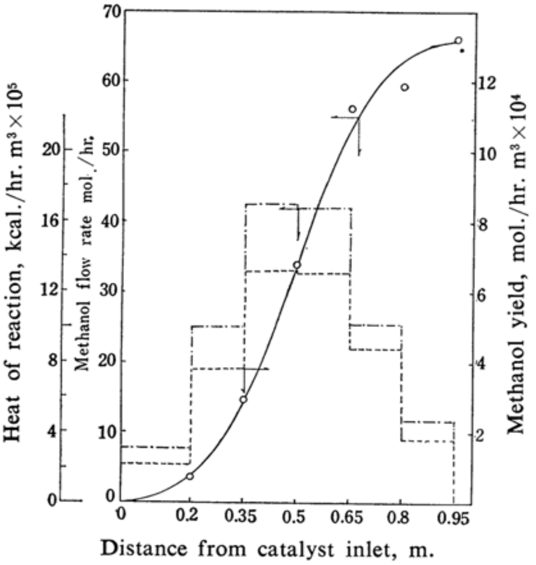

Fig. 6. Methanol flow rate, methanol yield and reaction heat of methanol synthesis as function of bed length. Exp. 1.
—○— Methanol flow rate
-------- Methanol yield
—·—· Heat of reaction

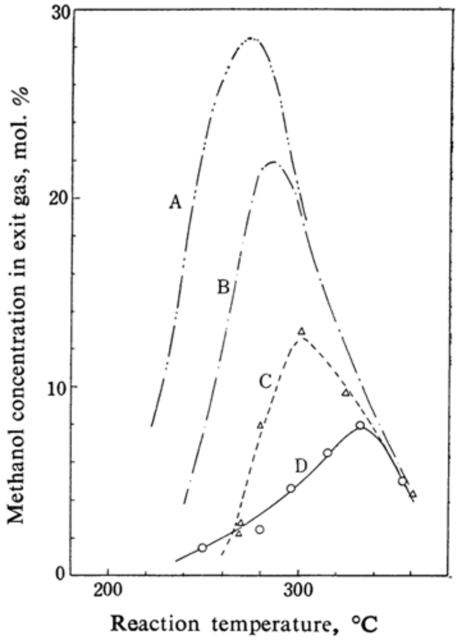

Fig. 7. Catalyst activity for methanol synthesis.
—·— Activity after reduction at 250°C
—·—· Activity after heating at 360°C
---△--- Activity after heating at 450°C
—○— Activity after runs 1—10

Discussion

Calculation of Temperature Profiles.—The heat balance equation for a tubular reactor packed with catalyst granules is given generally as

$$C_pG\frac{\partial t}{\partial x}=\frac{1}{r}\left\{\frac{\partial}{\partial r}\left(\lambda_r\cdot r\frac{\partial t}{\partial r}\right)+\frac{\partial}{\partial x}\left(\lambda_x\cdot r\frac{\partial t}{\partial x}\right)\right\}+Q \qquad (1)$$

where C_p is the heat capacity of the fluid, G is the mass velocity based on an empty tube,

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5) W. J. Thomas, *Ind. Eng. Chem.*, **50**, 967 (1958).

6) H. Uchida and Y. Ogino, This Bulletin, **31**, 45 (1958).

t is the over-temperature in the catalyst bed (which is defined by $t_b - t_w$, where t_b is the bed temperature and t_w is the temperature of heat transfer medium), x is the distance from the catalyst inlet, λ_x and λ_r are the respective thermal conductivities of the bed in the axial and lateral directions, and Q is the heat of the reaction. Strictly speaking, Q in Eq. 1 is to be given as a function of the reaction rate, and hence as a function of the temperature and concentration. For the sake of simplicity, the reaction heat was sometimes approximated to a function of x alone, and Eq. 1 was solved after this substitution. This approach was made by Kodama and Fukui, by Shindo, by Maeda, by Kjaer, and by Kuraishi et al., who have proposed the following formulae: $Q = q_0 e^{-cx}$ with $\lambda_x = \lambda_r$[7], or with $\lambda_x \neq \lambda_r$[8], $Q = Ae^{-cx} + B$[9], and $Q = c_1 e^{-Mx} + c_2 e^{-Nx}$[2], where q_0 is the reaction heat at the catalyst inlet and c, A, B, c_1, c_2, M, and N are constants conveniently chosen to fit the profile of the reaction heat. None of the above formulae, however, could express the present axial distribution data of the reaction heat. The solution of Eq. 1 along this line has, therefore, been given up, and a more simplified method, a step by step calculation of the temperature profile, has been adopted. In this method, the total bed length is divided into steps, and throughout each of the steps the heat of the reaction is assumed to be constant.

Under the further assumptions that the catalyst bed is cylindrical[10] and that λ_x and λ_r are identical and equal to λ_e, the solutions of the heat balance equations for the individual steps with the following boundary conditions,

$$(t_i)_{x=0} = t_{0i} - t_w, \quad (\lambda_e \partial t_i / \partial r + U t_i)_{r=R} = 0$$

are summarized by Eq. 2:

$$t_i = (t_i)_{x_i=0} \sum_{n=1}^{\infty} \frac{2J_0(a_n r/R) e^{-\alpha^2 y}}{a_n (1 + a_n^2/b^2) J_1(a_n)} + (Q_i/\lambda_e) \sum_{n=1}^{\infty} \frac{(R/a_n)^2 2J_0(a_n r/R)(1 - e^{-\alpha^2{}_n y})}{a_n (1 + a_n^2/b^2) J_1(a_n)} \tag{2}$$

in which the following abbreviations are introduced:

$$b = UR/\lambda_e, \quad A = (\lambda_e / C_p G)^2, \quad \text{and} \quad y = \lambda_e x_i / C_p G$$

In the above equations, t_i is the bed over-temperature, t_{0i} is the bed temperature at the top of the ith step ($x_i = 0$), R is the inner radius of the reactor tube, and U is the overall heat transfer coefficient, which is based upon the temperature difference between the catalyst bed at $r = R$ and the heat transfer medium and which is referred to the inner diameter of the reactor. Further, a_n's and α_n's are the positive roots of the following auxiliary equations, $a_n J_1(a_n) = b J_0(a_n)$ and $A\alpha_n^4 + \alpha_n^2 - a_n^2/R^2 = 0$, respectively. J_0 and J_1 are Bessel functions of the first kind, zero and first order respectively.

In the calculation of t by Eq. 2, the constants, such as C_p, k (the thermal conductivity of fluid) and μ (the viscosity of fluid), are evaluated in the sampe way as has been described elsewhere[1]; from k and μ thus obtained, λ_e is determined by the aid of the formula proposed by Hatta and Maeda[11]. U is usually defined by the equation:

$$1/U = 1/h + (1/h_L)(R/R_O) + (R/\lambda_s) \ln R_O/R \tag{3}$$

where h and h_L are the heat transfer coefficients referred to the inner and outer tube surfaces respectively, λ_s is the thermal conductivity of the reactor tube material, and R_O is the outer radius of the reactor tube. However, the evaluation of U is impossible, because the characteristic constants of the heat transfer medium, and consequently of h_L, are not available. As it is, a trial and error method has been adopted for the determination of U, as is described in the next paragraph.

The step lengths used in the calculation of the temperature profiles are 0.2 m. for the first step and 0.15 m. for the other steps; the Q_i corresponding to each step is found in Fig. 6. Furthermore, it should be noted that the application of Eq. 2 to the step by step calculation is permissible only if the radial temperature profile is uniform at the top of each step (cf. footnote 13). This, however, is not the case with the present experimental profiles. A more conventional procedure is, therefore, adopted to calculated the axial profile based on the average temperature over a cross section. Under the assumption that the catalyst inlet

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[7] S. Kodama and K. Fukui, *Chem. Eng. (Kagaku Kikai)*, **14**, 259 (1950); S. Shindo, *Memoir Muroran Univ. Eng.*, **1**, 51 (1950).

[8] S. Maeda, *Chem. Eng. (Kagaku Kogaku)*, **19**, 212, 263 (1955).

[9] L. Kjaer, "Measurement and Calculation of Temperature and Conversion in Fixed-bed Catalytic Reactors", Jul. Gjellerups Vorlag, Copenhagen (1958), p. 85.

[10] The assumption is rather conventional. A similar solution of Eq. 1 for an annular-shaped cylindrical bed, through which passes a thermocouple tube, and a calculation of t by the aid of the solution were also made. The results have proved to be almost identical with those obtained by the use of Eq. 2. The cooling effects due to the other thin tubes placed in the bed are conventionally ignored in the present calculations.

[11] $\lambda_e/k = 0.209(R_{ep})^{0.87}$, $R_{ep} = d_p G/\mu$, where R_{ep} is the modified Reynolds number, d_p is the diameter of catalyst granules (cf. footnote 12).

[12] S. Hatta and S. Maeda, *Chem. Eng. (Kagaku Kikai)*, **12**, 56 (1948).

[13] M. Shindo and H. Kubota, ibid., **19**, 487 (1955).

TABLE II. THERMODYNAMICAL DATA, OVERALL HEAT TRANSFER COEFFICIENT AND OTHER MATTERS

Exp.	C_p kcal./kg.°C	μ kg./m.hr.	k kcal./m.hr.°C	λ_e kcal./m.hr.°C	G kg./m²hr.	R_{ep}	U kcal./m²hr.°C
1	0.9987	0.0793	0.2548	6.528	5.698×10^3	2.515×10^2	2.912×10^2
7	1.0934	0.0768	0.2605	3.814	2.901×10^3	1.322×10^2	2.912×10^2
9	0.8703	0.0824	0.2479	7.930	7.642×10^3	3.246×10^2	2.912×10^2

temperature is radially uniform with an arithmetically average temperature of the three experimental temperatures, the calculation of t at the end of the first step by the aid of Eq. 2 leads to a radial profile which is reduced to an average temperature over the cross section[14]. The average temperature is, then, assumed to be equal to that at the top of the second step; the same calculation is repeated as regards the second step, and so forth. In the calculation, a value of U was chosen in order that the calculated average temperature might fit the experimental temperature based on the arithmetically average one of Exp. 1 as closely as possible. The value of U thus obtained is given in Table II, together with the other constants. The procedure was then applied to the data of Exps. 7 and 9 as well as of Exp. 1; the resultant average temperatures are plotted as a function of the bed length in Fig. 8. For the sake of comparison, the figure includes the experimental profiles based on the arithmetically average temperature. The comparison shows that the profiles are almost, though not entirely, consistent with each other.

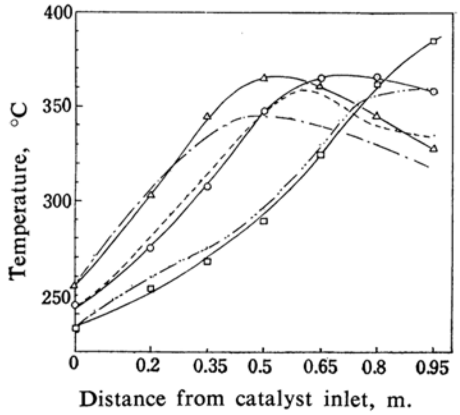

Fig. 8. Comparison between experimental and calculated profiles based on average temperature over cross section.

—○— Experimental Exp. 1
—△— Experimental Exp. 7
—□— Experimental Exp. 9
--------- Calculated Exp. 1
—·—· Calculated Exp. 7
—··— Calculated Exp. 9

This, however, may be the order of accuracy to be expected in the present performance data.

On the basis of the experimental facts in Exp. 1 that the radial temperature profile happens to be flat at a cross section 0.35 m. from the catalyst inlet and that the Q_i's are nearly equal between the third and the fourth steps (cf. Fig. 6), Eq. 2 may be applied to the calculation of the radial temperature profiles over cross sections within these steps. The calculated profiles are shown in Fig. 5. The discrepancy between the experimental and calculated profiles is small at the cross section very near the top of the third step, but it tends to increase to some extent with the increasing bed length.

Once U has been obtained for the present synthesis, h_L, in turn, is obtained from Eq. 3, since h in the equation can be calculated from the formula of Hatta and Maeda[15]. The values of h_L thus obtained are listed in Table III, together with those of U, h, and λ_s. By the use of these values, radial temperature profiles in the range from the bed at $r=R$ to the heat transfer medium can be drawn in the same way as has been reported previously[2]. Sample profiles are given in Fig. 5 for Exp. 1. The figure, like the table, clearly indicates that the heat transfer resistance is largest at the outer tube surface.

TABLE III. HEAT TRANSFER CONSTANTS

Exp.	h kcal./m²hr.°C	h_L kcal./m²hr.°C	λ_s kcal./m.hr.°C
1	2.797×10^3	2.091×10^2	2.530×10
7	2.859×10^3	2.084×10^2	2.530×10
9	2.722×10^3	2.099×10^2	2.530×10

Optimum Reaction Temperatures.—The determination of the optimum reaction temperature, at which the maximum rate of methanol synthesis is attained, is of interest in estimating the optimum operation conditions for a reactor. The determination can be conducted by the aid of a chart in which lines of constant conversion, with reaction rates as ordinates and temperatures as abscissas, are drawn.

As has been stated previously[4], the rate of

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[14] The average temperature t_{av}, is calculated by means of the equation: $t_{av}=\int_0^R 2\pi r t\,dr/\pi R^2$.

[15] $hD/\lambda_e=254(R_{ep}d_p/D)^{-0.87}$, where D is the equivalent diameter of the catalyst bed (cf. footnote 12).

methanol synthesis is represented by the following equation:

$$r=k_{\mathrm{d}}(a_{\mathrm{CO}}a^2_{\mathrm{H_2}})^{0.7}\ (1-a_{\mathrm{CH_3OH}}/Ka_{\mathrm{CO}}a^2_{\mathrm{H_2}}) \qquad (4)$$

Upon substitution of the following relation for the reaction rate in a fixed-bed reactor, $r=(273\,\boldsymbol{R}c_{\mathrm{m}}A)^{-1}\cdot \mathrm{d}F/\mathrm{d}x$, and subsequent rearrangement, Eq. 4 is rewritten as:

$$k=273\,\boldsymbol{R}c_{\mathrm{m}}k_{\mathrm{d}}=(\mathrm{d}F/A\mathrm{d}x)/(a_{\mathrm{CO}}a^2_{\mathrm{H_2}})^{0.7} \times(1-a_{\mathrm{CH_3OH}}/Ka_{\mathrm{CO}}a^2_{\mathrm{H_2}}) \qquad (5)$$

In the equation, k_{d} is the rate constant, $\boldsymbol{R}$ is the gas constant, a is the activity, c_{m} is the mean compressibility coefficient of gas at a normal state, K is the equilibrium constant of methanol synthesis, F (m^3 (N. T. P.)/hr.) is the flow rate of methanol, and A is the cross sectional area of the bed. By the aid of Eq. 5, k at any x is calculated from experimental data, for instance, from the data of Fig. 6. Furthermore, one can draw an Arrhenius' plot of k, because the average temperature over a cross section at the x is determined from the experimental radial temperature profile. The plot is shown in Fig. 9, where an approximate activation energy of the methanol synthesis is found to be 15 kcal./mol. From combining the rate constants with the activation energy thus obtained, the rates at various methanol concentrations and temperatures in Exp. 1 are calculated by Eq. 4, and the resultant data are plotted in Fig. 10 as the lines mentioned above. This chart is restricted to a pressure of 200 kg./cm^2 of the synthesis gas, with a fixed composition and flow rate corresponding to those of Exp. 1. In the figure, the maximum rate curve, which indicates the most favorable temperature profile in the catalyst bed, is given by a thick broken-line curve, whereas the experimental rate curve is given by a thick solid-line curve. Comparison of the two curves discloses that. for attaining the efficient performance of the reactor, the temperature in the zone of low methanol concentration, or in the top zone of the catalyst bed, is too low, whereas the temperature in the zone of high methanol concentration, or in the bottom zone, is too high.

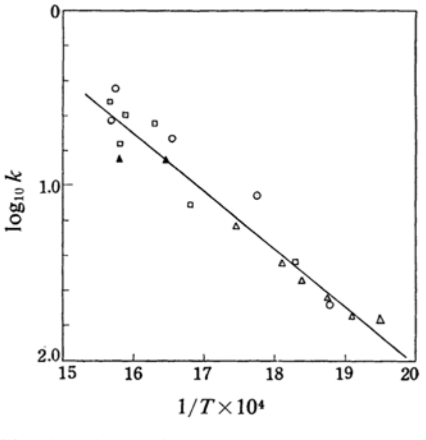

Fig. 9. Arrhenius' plot of rate constant.
○ Exp. 1 □ Exp. 7 ▲ Exp. 9
△ After use in runs 1—10 (refer to Fig. 7)

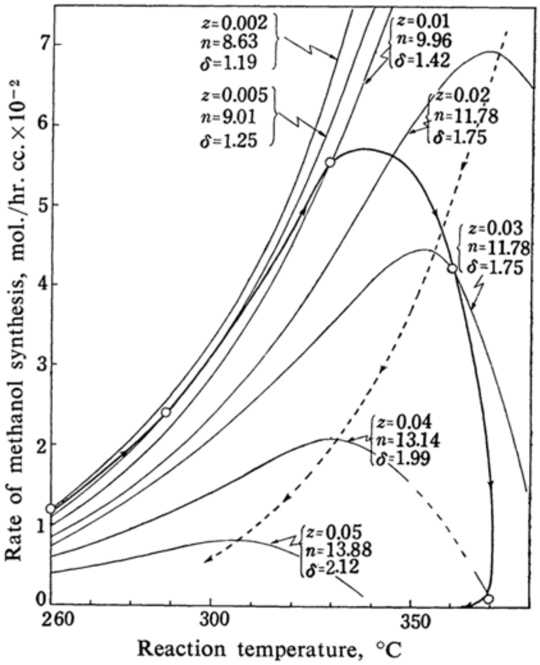

Fig. 10. Effect of temperature and conversion on rate of methanol synthesis.
------ Maximum rate curve
—— Rate curve for Exp. 1
z, methanol concentration $n=\mathrm{H_2/CO}$, $\delta=$inert gas/CO

If the heat transfer referred to the outer tube surface is improved, the axial temperature profile could be more uniform, becoming higher in the top zone and lower in the bottom zone, and, as a consequence, the experimental rate curve would approach the maximum rate curve. Nevertheless, this improvement alone would not necessarily diminish the large magnitude of the temperature rise in the catalyst bed. With the increasing methanol output, the magnitude is liable to increase more considerably in the bottom zone. An alternate means of providing a suitable control of the bed temperature is the use of a heat exchanger in the catalyst bed, by which the temperature could be controlled by radial heat transfer through the bed. The effect of a heat exchanger on the bed temperature profile, and consequently on the reactor performance, will be described in our next paper.

Summary

On the basis of the experimental concentration and temperature profiles for one of the synthesis runs, the experimental rate curve has been drawn on a chart in which lines of constant conversion with reaction rates are given as ordinates and temperatures as abscissa. In a step by step calculation of the temperature profiles from the experimental profiles by the use of a set of analytical solutions of the heat balance equation, which includes the respective constant reaction heat terms given by the step by step distribution plot, the heat transfer coefficients are conveniently chosen to match the calculated profiles with the experimental ones. Taking the heat transfer efficiencies thus obtained into consideration, a comparison of the experimental rate curve with the maximum rate curve on the afore-mentioned chart discloses that, for attaining an efficient performance of the reactor, not only should the heat transfer referred to the outer tube surface be improved, but also the temperature rise in the catalyst bed should be controlled by a suitable means.

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