Fischer-Tropsch Synthesis with Tubular Reactor of 18.1 l. Catalyst Bed. I. Reactor with Constant Temperature Wall

By Michio KURAISHI*, Minoru KURITA, Tadasuke HOSOYA, Hideo ICHINOKAWA, Kiyoshi OGAWA and Hiroshi UCHIDA

(Received September 13, 1960)

In our previous paper¹⁾ dealing with the Fischer-Tropsch synthesis in a tubular reactor, a procedure for calculating temperature profiles from experimental concentration gradients of components along the reactor was proposed. The procedure was developed by making use of experimental data available with the reactor which contained a catalyst bed of 2 l., and which was held in a circulating oil bath at a constant temperature. Under the assumption that situations in the synthesis are similarly realized independently of the sizes of the reactor, the procedure promises that we may foresee performances of reactors of a larger size. Along this line of expectation, precalculations of temperature profiles are made for the synthesis with any reactor of similar construction but about ten times as large as the previous one. The applicability of the procedure may then be checked by comparing the results of precalculation with the experimental temperature profile in the synthesis with the present reactor of the larger size. Moreover, the same procedure is followed to give the temperature profiles from the experimental concentration gradients along the present reactor.

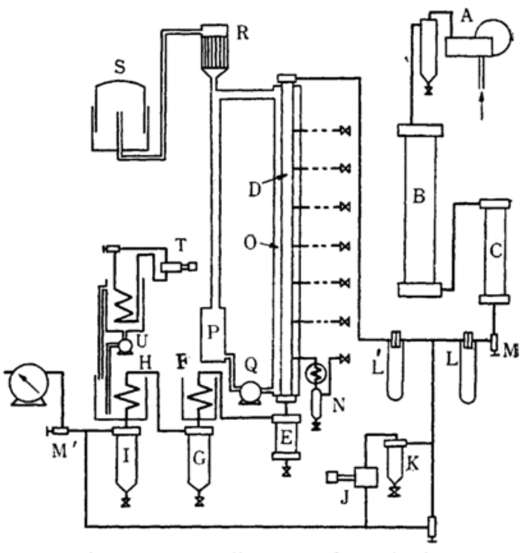

Fig. 1. Flow diagram of synthesis.

A, Gas compresser
B, Pressure reservoir
C, Desulfrizer
D, Reactor
E, Hot separator
F, Water cooler
G, Cold separator
H, Brine cooler
I, Cold separator
J, Gas circulating pump
K, Oil separator
L, L', Flow meter
M, M', Reducing valves
N, Cold separator
O, Oil bath
P, Hot oil reservoir
Q, Hot oil pump
R, Condenser
S, N_2 gas holder
T, Refrigerator
U, Brine pump

Experimental

Raw water-gas for the synthesis is produced from coke and steam by the usual procedure. Hydrogen sulfide and carbon dioxide in the gas are removed in a gas purification train consisting of a sodium carbonate solution washer, an iron oxide box, and finally a caustic soda solution washer. The gas is then compressed at about 100 kg./cm^2 into a high pressure gas storage of 2000 l. (B), from which the compressed gas is introduced into a synthesis unit through a vessel (C) containing active charcoal for removal of organic sulfur. As shown in Fig. 1, the synthesis unit consists of a reactor (D), two hot separators (E), two cold separators (G) with

---

* Present address: Japan Gas Chemical Co., Enoki-cho, Niigata.

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

coolers (F), a low temperature separator (I) with a cooler (H), and a gas circulating pump (J) equipped with an oil separator (K), every one of which is of a design similar to, but about ten times as large as the corresponding equipment in the previous plant1). Having been mixed with part of the end-gas from the low temperature separator, an amount of the fresh gas is fed through a flow meter (L) into the reactor top where it flows in a downward direction through the catalyst bed. The volume of the fresh gas thus introduced is estimated from the degree of pressure decrease in the pressure gas storage and the flow rate is controlled by means of are ducing valve (M) and a flow meter (L). The volume of the fresh gas having been once estimated, one can easily calculate the flow rate of the circulating gas from carbon dioxide balance between the gases after and just before the reactor. Part of the gas after being separated at the low temperature separator is purged through a reducing valve (M′). In the above estimation, the volume of the gas thus purged is to be taken into account.

The reactor is 70 mm. in outer diameter and 50 mm. in inner diameter by 10 m. high2), and is a simple reactor type with a constant temperature wall, being placed coaxially in a cylinder of oil (Dowtherm) bath (O). Into the bottom of the cylinder hot oil is fed at the flow rate of 2.5 m^3/hr., and flows upwards through an annular space between the cylinder wall and the reactor to the top, where the oil is allowed to flow down to a hot oil reservoir (P) which is being kept at a definite temperature. The recycling system of hot oil is always enclosed in an atmosphere of nitrogen which is supplied from a nitrogen gas holder (S) through an oil condenser (R).

The reactor contains a bed of 18.1 l. reduced catalyst (37.06 kg.). Two coaxial thermocouple wells 5 m. in length, 10 mm. in outer diameter, and 5 mm. in inner diameter, either one of which is fixed at the top or the bottom cover, go through the catalyst bed, and scanning of the temperature profile along the whole length of the reactor is made by moving the thermocouples in the wells. From seven successive ports at different heights along the catalyst bed, all of which are 1.2 m. apart from each other, a small portion of the fluid is withdrawn through a small cold separator (N) to be freed of water and oil, and the residual gaseous mixture is analyzed for the compositions. From the results of the analyses together with weighed amounts of the water, concentration gradients of the individual components along the catalyst bed are determined.

A sintered catalyst has been employed in the present synthesis. It was prepared, according to the procedure reported in our previous paper4), from powders of a fused iron oxide catalyst containing in parts by weight 93.25 Fe_3O_4, 3 Al_2O_3, 1 CaO, 1 MgO, 1 WO_3, 0.25 CuO and 0.5 K_2O. The catalyst powders less than 100 mesh in size were pressed into tablets of 4×4 mm., which were sintered at 1000°C for one hour. Before use in the synthesis, the finished catalysts were completely reduced in a separate oven in a current of hydrogen at 500°C, and were removed from the oven to be packed into the synthesis reactor in carbon dioxide atmosphere.

Prediction of Temperature Profile

Among the synthesis experiments with the reactor of 2 l. catalyst bed (25 mm. I. D.)1), Exp. No. 6 showed that a temperature difference of 24°C appeared between the oil bath and the center across the bed during the synthesis where by using a sintered catalyst5) a product (oil plus wax) yield of 2.72 kg./day was obtained under the following synthesis conditions: the pressure was 25 kg./cm^2, and the space velocities based on the recycle and the fresh gases were 1975 and 763, respectively. This makes us feel uncertain whether a smooth operation of the synthesis can be made with the present reactor, since the temperature in the present synthesis may be liable to rise too high. In this connection, a preliminary calculation is made to predict the temperature rise. The precalculation is made by the aid of the procedure proposed by us1), being combined with reasonable assumptions on the synthesis for the scaled-up reactor.

Heat transfer in a catalyst bed packed in a single tubular reactor is generally given by the following equation,

$$C_pG\frac{\partial t}{\partial x}=\frac{1}{r}\left\{\frac{\partial}{\partial r}\left(\lambda_r\cdot r\frac{\partial t}{\partial x}\right)+\frac{\partial}{\partial x}\left(\lambda_x\cdot r\frac{\partial t}{\partial x}\right)\right\}+\sum v_i q_i \tag{1}$$

with the following boundary conditions,

$$\left.\begin{aligned}&[t]_{x=0}=t_0\\&\left[\lambda_r\frac{\partial t}{\partial r}+Ut\right]_{r=r_2}=0\\&\left[\frac{\partial t}{\partial r}\right]_{r=r_1}=0\end{aligned}\right\} \tag{2}$$

where C_p is the heat capacity per unit mass of fluid, G is the mass velocity, t is the temperature difference between a catalyst bed and an oil bath, x is the distance from the top of the bed, r is the distance in lateral direction, λ is the effective thermal conductivity of the catalyst bed fluid system, v is the reaction rate, q is the reaction heat, U is the overall heat transfer coefficient, r_1 and r_2 are the inner and the outer radii of the catalyst bed, respectively.

---

2) According to the paper by Tramm3), a great number of the reactors of this size are placed in an oven for the Industrial synthesis.

3) H. Tramm, a paper presented at the Fifth World Petroleum Congress, Section III (1959).

4) H. Uchida and H. Ichinokawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **58**, 563 (1955).

5) The sintered catalyst used in the previous study was prepared from powders of a fused iron oxide catalyst containing in parts by weight 94 Fe_3O_4, 4 Al_2O_3, 1 CaO and 1 K_2O.

The last term in the right side of Eq. 1 concerns heat quantities of the reaction. It is usually determined according to a rate equation of the synthesis, and is a function of temperature and concentration. However, our previous work[1] pointed out that the term could be approximated to the following formula[6].

$$\sum v_i q_i = Q(\text{kcal./m}^3\text{ hr.}) = c_1 e^{-Mx} - c_2 e^{-Nx} \qquad (3)$$

where Q stands for the heat evolved per hour in unit volume of the catalyst bed at a distance x from the top, and c_1, c_2, M and N are constants. Numerical values of the constants could then be determined from the distribution curve of the reaction heat given as a function of x. In this respect our previous paper[1] stated details of drawing the curve on the basis of experimental concentration gradients along the reactor.

Substitution of Eq. 3 into Eq. 1 and subsequent solution of the resulting equation result in the following formula,

$$\begin{aligned} t = t_0 \sum_1^{\infty} & \frac{2U_1(a_n)U_0(a_n r/r_2)\exp(-\alpha_n^2 y)}{\begin{pmatrix} a_n[\{1+(a_n^2/b^2)\}U_1^2(a_n) \\ -(r_1/r_2)^2 U_0^2(a_n r_1/r_2)] \end{pmatrix}} \\ & + \sum_1^{\infty} \frac{2U_1(a_n)U_0(a_n r/r_2)}{\begin{pmatrix} a_n[\{1+(a_n^2/b^2)\}U_1^2(a_n) \\ -(r_1/r_2)^2 U_0^2(a_n r_1/r_2)] \end{pmatrix}} \\ & \times \left\{ \frac{[c_1(\exp(-my)-\exp(-\alpha_n^2 y))]}{[\lambda_r(a_n^2/r_2^2 - m - \lambda_x M^2/\lambda_r)]} \right. \\ & \left. - \frac{[c_2(\exp(-ny)-\exp(-\alpha_n^2 y))]}{[\lambda_r(a_n^2/r_2^2 - n - \lambda_x N^2/\lambda_r)]} \right\} \qquad (4) \end{aligned}$$

$$U_0(a_n r/r_2) \equiv J_0(a_n r/r_2) - cY_0(a_n r/r_2)$$

$$U_1(a_n r/r_2) \equiv J_1(a_n r/r_2) - cY_1(a_n r/r_2)$$

$$\begin{aligned} C &\equiv J_1(a_n r_1/r_2)/Y_1(a_n r_1/r_2) \\ &= [a_n J_1(a_n) - bJ_0(a_n)]/[a_n Y_1(a_n) - bY_0(a_n)] \end{aligned}$$

In Eq. 4 a_n and α_n stand for roots of equations $a_n U_1(a_n) = aU_0(a_n)$ and $A\alpha_n^4 + \alpha_n^2 - a_n^2/r_2^2 = 0$, respectively. In addition, there are following relations,

$$A \equiv \lambda_x \lambda_r/(C_p G)^2, \quad b \equiv Ur^2/\lambda_r, \quad y \equiv \lambda_r x/C_p G,$$

$$m \equiv MC_p G/\lambda_r \text{ and } n \equiv NC_p G/\lambda_r.$$

J_0 and J_1 are Bessel functions of first kind, zeroth and first order, respectively, and Y_0 and Y_1 are the same functions of second kind, zeroth and second order, respectively.

Let us calculate t with the present reactor by the aid of Eq. 4. Before proceeding to the calculation, it is assumed that the same synthesis conditions as these for Exp. No. 6 with the previous reactor hold again for the predicted synthesis, and that the same situations are realized in the predicted synthesis as were realized in the previous Exp. No. 6. Under these assumptions, the flow rate of the gaseous components and the yield of the product (oil plus wax) are 18.1/2 times as great as they were in Exp. No. 6. Hence the product yield attains 24.6 kg./day, and the flow rate of the gaseous components is 30 kg./hr.. Modified Reynolds number ($R_{\text{ep}} = d_p G/\mu$) takes a value of 7.22×10^2, where d_p is 4 mm. Characteristic constants, such as the specific heat (C_p), the viscosity (μ), and the thermal conductivity (k) of the fluid are determined in the following manner where compromise averages are taken between these based on the inlet and the exit gases. This results in the following values of $C_p = 0.42$ kcal./kg.°C, $\mu = 0.088$ kg./m. hr. and $k = 0.088$ kcal./m. hr.°C, respectively.

Moreover, the following values of the heat transfer constants are obtained as regards the predicted synthesis: $\lambda = 5.65$ kcal./m. hr.°C (2.61), $h = 866$ kcal./m² hr. °C (1086), and $h_L = 174$ kcal./m² hr. °C (120)[10], where h and h_L are the tube wall coefficients of heat transfer based on the inner and the outer surfaces of the reactor, respectively. Numericals in the brackets give the corresponding values for Exp. No. 6 with the previous reactor. As a consequence, a higher value of the overall heat transfer coefficient (U), which is 184 kcal./m² hr. °C as compared with 160 kcal./m²·hr. °C in Exp. No. 6, is obtained. Anyhow, the in crease in the value of U is mainly due to the higher value of h_L in the predicted synthesis.

The constants in Eq. 3 have remained undetermined as yet. In interpretation of the data of Exp. No. 6, they were evaluated to be

$$\begin{aligned} Q(\text{kcal./m}^3\text{ hr.}) &= 6.12 \times 10^5 e^{-0.18x} \\ &\quad - 4.99 \times 10^5 e^{-1.01x} \end{aligned} \qquad (5)$$

The length of the reactor being denoted by L, the equation can be rewritten

$$\begin{aligned} Q(\text{kcal./m}^3\text{ hr.}) &= 6.12 \times 10^5 e^{-0.82x/L} \\ &\quad - 4.99 \times 10^5 e^{-4.60x/L} \end{aligned} \qquad (6)$$

since L for the previous reactor was 4.55 m. Eq. 6 can represent the distribution of the reaction heat independently of the dimensions of the reactor, provided that the synthesis proceeds with the same tendency as that which took place in Exp. No. 6, namely that the

---

6) Kodama et al.[7], Shindo[8], and Maeda[9] had already given the exprssion of $\sum v_i q_i = ce^{-kx}$.

7) S. Kodama and K. Fukui, *Kagaku Kikai*, **12**, (1948).

8) M. Shindo, *Memoir Muroran Univ. Eng.*, **1**, 51 (1950).

9) S. Maeda, *Kagaku Kikai*, **15**, 5 (1951).

10) λ and h have been evaluated by using the formula by Hatta et al.[11], while h_L has been evaluated by using the formula recommended by McAdams[12].

11) S. Hatta and S. Maeda, *Kagaku Kikai*, 13, 79 (1949).

12) W. H. McAdams, "Heat Transmission", McGraw Hill Co. New York (1954).

heat evolving within unit volume of the catalyst bed at a value of x/L is equal to the corresponding one in Exp. No. 6. The constants for the predicted synthesis are then given by putting $L=9.6$ m. in Eq. 6, which follows

$$Q(\text{kcal./m}^3\text{ hr.}) = 6.12\times10^5 e^{-0.085x} - 4.99\times10^5 e^{-0.48x} \qquad (7)$$

For the sake of convenience, a graphical representation of the results is given in Fig. 2 (curve A) as a plot of q (kcal./m. hr.), which is defined by $q=Q/\pi(r_2^2-r_1^2)$, against x. According to the definition, q stands for the reaction heat evolved in an hour within the catalyst bed occupying the unit length of the reactor.

By putting the above numerical values of the constants into Eq. 4, the temperature profile either along or across the catalyst bed can be drawn, as shown in Fig. 2 (curves B and B′). The curves indicate that in the predicted synthesis with the present reactor the temperature difference between the oil bath and the center cross the catalyst bed attains only 31.5°C at the highest. Considering that the temperature difference in Exp. No. 6 was 24°C, and that the reaction heat evolving within a volume occupying the unit length of the present reactor becomes about fourtimes[13] as great as the heat with the previous reactor, the difference appears rather small.

We experienced the fact that with the previous reactor the synthesis could be carried out without serious difficulties, even when the temperature difference between the oil bath and the catalyst bed attained as high as 49°C (refer to Exp. No. 5 in our previous paper[1]). Based on the magnitude of predicted temperature rise, an operation of the synthesis with the present reactor may be expected to be probable.

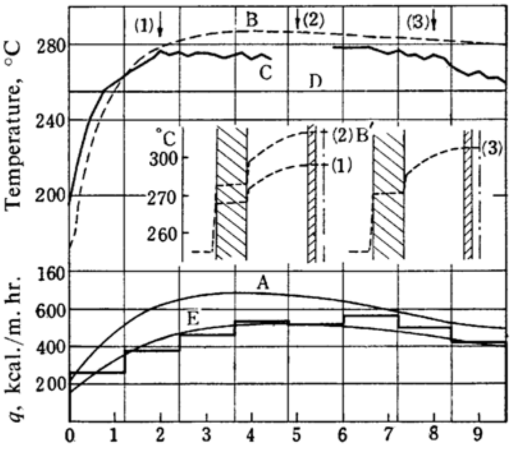

Fig. 2. Above, predicted and experimental temperature profiles. Below, distribution of q.

A, Predicted distribution of q
B, B′, Predicted temperature profile (B, axial, B′, radical)
C, Experimental temperature profile
D, Oil bath temperature
E, Experimental distribution of q

In the drawing of curves B′, the magnitude of temperature rise from the oil bath to the outer wall-surface of the reactor (t_{wo}) and that to the inner wall-surface (t_{w1}) are given by the respective following formulae of the heat balance,

$$t_{\text{wo}}=t_{r=r_2}r_2U/r_3h_L, \quad t_{\text{w1}}=t_{r=r_2}(1-U/h)$$

where r_3 is the outer radius of the reactor.

Results and Discussion

Experimental Results. — The synthesis was made under the operating conditions as cited in Table I. The table also includes the operating conditions, product yield, and other points

TABLE I. SYNTHESIS CONDITIONS, CONVERSION, PRODUCT YIELD, AND OTHER MATTERS WITH THOSE OF PREDICTED SYNTHESIS

	Pressure kg./cm²	Oil bath temperature °C	Space velocity, hr⁻¹		Volume contract %
			Base on fresh gas	Based on recycle gas	
Exp.	30	255	620	2070	42.2
Predicted	25	255*	763	1975	43.1
	Oil plus wax kg./day	Water kg./day	Oil plus wax per (H_2+CO) m³	Use ratio (H_2/CO)	Recycle ratio
Exp.	14.42	22.65	99.4	1.074	2.35
Predicted	24.62	19.10	130.5	0.819	1.59

* In the prediction of the temperature profile, wit as needless to consider the oil bath temperature, while for a convenient comparison of the predicted profile with the actual one curve A in Fig. 2 is drawn on the basis of the oil bath temperature of 255°C.

---

[13] Strictly speaking, the heat is $(25^2-5^2)/(12.5^2-4^2)$ times in amount, where the numerals 5 and 4 are radii (mm.) of the thermocouple wells in the present and the previous reactors, respectively.

for the predicted synthesis. In the synthesis a much lower yield of oil plus wax[14] has been obtained with a greater amount of water than was predicted. As naturally expected from the lower yield, the actual temperature profile lies lower than the predicted profile (refer to Fig. 2). It may be noted, however, that the shape of the predicted profile is very similar to the actual profile except that the actual one is higher by 20°C at the topzone of the catalyst bed.

Calculation of Temperature Profile from Concentration Gradient.—Figure 3 shows the determined concentration gradients of reactants (H_2, CO) and products (H_2O, CO_2, et al.) as a function of distance from the top along the catalyst bed. Our previous paper[1,15] reported that amounts of carbon monoxide consumed either by the hydrocarbon synthesis according to consecutive reactions of $H_2+CO \rightarrow >CHOH$ and $>CHOH+H_2 \rightarrow -CH_2-+H_2O$ or by the water-gas shift[17,18] could be estimated from the concentration gradients, and the same procedure is now followed to result in Fig. 4. As soon as the carbon monoxide consumptions have been determined, magnitudes of the reaction heat can easily be calculated by taking theoretical quantities of the reaction heat into consideration. The quantities are 1.86 kcal./l. $CO_{consumed}$ and 0.41 kcal./l. $CO_{consumed}$ for the reaction heats with the hydrocarbon synthesis and the water-gas shift, respectively. The results are given in Fig. 5 as a stepwise plot (steplength, 1.2 m.) of the heat evolved per volume occupying unit length of the catalyst bed against the bed length. From the plot one can evaluate the constants in Eq. 3 to give $c_1=5.84\times10^5$, $c_2=5.05\times10^5$, $M=0.095$, and $N=0.35$. On the other hand, the other constants included in Eq. 4 have been evaluated on the basis of the actual synthesis conditions, which

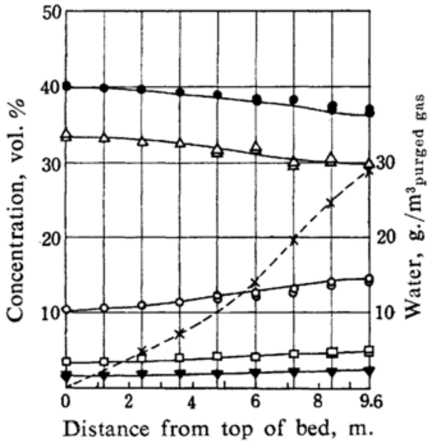

Fig. 3. Concentration gradients and amounts of water produced as a function of x.

—●— Hydrogen
—△— Carbon monoxide
—○— Carbon dioxide
—□— Gaseous paraffin
—▼— Gaseous olefin
--×-- Water

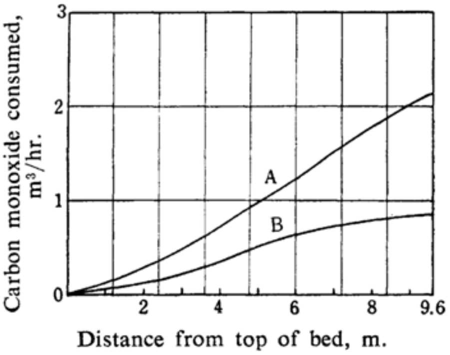

Fig. 4. Carbon monoxide consumptions.

A, By the hydrocarbon synthesis
B, By the water-gas shift reaction

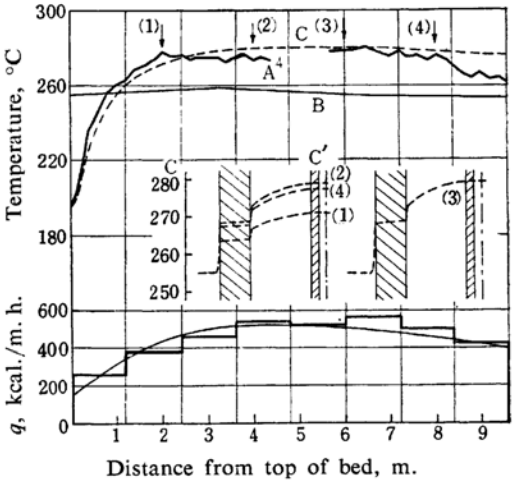

Fig. 5. Above, predicted and experimental temperature profiles. Below, distribution of q.

A, Experimental temperature profile
B, Oil bath temperature
C, C′, Temperature profiles calculated from experimental concentration gradients
D, Experimental distribution of q

---

[14] The lower yield may have been partly owing to the poisoning of the catalyst with organic sulfur in the raw gas, since the capacity of active charcoal was insufficient to maintain the sulfur content less than 1~2 mg./m³ throughout the period of the synthesis.

[15] Refer to the paper by Anderson et al.[16] also.

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

[17] H. Koelbel and F. Engelhartdt, *Chem. Ing. Tech.*, 22. 27 (1950).

[18] R. B. Anderson et al., *Ind. Eng. Chem.*, **44**, 391 (1952).

appear to be: $C_p=0.41$ kcal./kg.°C, $\mu=0.090$ kg./m.hr., $k=0.085$ kcal./m. hr. °C, $G=1.682\times10^4$ kg./m^2 hr., $R_{ep}=7.48\times10^2$ ($d_p=0.004$ m.), $\lambda=5.62$ kcal./m. hr.°C, $h=836$ kcal./m^2 hr. °C, $h_L=174$ kcal./m^2 hr. °C, and $U=183$ kcal./m^2 hr. °C.

The problem is to draw the temperature profiles. This can be done by putting the above numerical values into Eq. 4. The results are shown in Fig. 5 as the temperature profiles along and across the catalyst bed, of which the former profile agrees well with the actually determined one. We have thus been able to obtain the temperature profile from the experimental concentration gradient with the present reactor.

However, the reactor suffered from the following limitation, that temperature in the catalyst bed was liable to fluctuate, even though the output remained less than had been expected. This may have been brought about by a slight change in either the composition or the flow rate of the feed gas, fine control of which was difficult. As it is, temperature may rise so high until the catalyst bed beomes ignited with the increasing output, unless greater amount of the reaction heat is carried away from the catalyst bed. As expected from a higher value of h than that of h_L, the heat transfer encounters more difficulty at the outer surface area than at the inner surface area of the reactor. This is shown more substantially with the radial temperature profile in Fig. 5 (refer to 3 in the figure): namely, the temperature difference within the bed remains only 6.3°C at a reactor cross section which is 6 m. apart from the top, while the difference between the center and the oil bath attains as high a point as 24.1°C. For the more satisfactory operation of the synthesis it, therefore, is desired to improve the heat transfer referred to the outer surface area by any chosen device. The result with the reactor improved along this line will be reported in the next paper.

Summary

By the aid of the calculating procedure developed by us on the basis of experimental data available in the synthesis with the reactor of 2 l. catalyst bed, prediction of the temperature profile as regards the synthesis with the reactor of 18.1 l. catalyst bed has been made. The predicted temperature profile expresses the tendencies observed in the actual synthesis with the latter reactor, though a complete agreement has not yet been obtained because of a lower output than was expected.

The calculating procedure has been applied to draw the temperature profile on the basis of the present experimental concentration gradients along the reactor. The profile thus drawn agrees well with the measured one.

The authors are particularly indebted to Messrs. M. Oba, A. Matsuda and H. Imai for their assistance in the synthesis experiment.

Governments Chemical Industrial
Research Institute, Tokyo
Shibuya-ku, Tokyo