Fischer-Tropsch Synthesis with Tubular Reactor of 18.1 l. Catalyst Bed. II. Reactor with Temperature Gradient along Out-side Wall

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A previous paper¹⁾ in this series described the Fischer-Tropsch synthesis with the reactor whose out-side wall temperature was kept constant along the whole length by means of a heat transfer medium of flowing oil. However, the catalyst bed temperature tended to rise very high, and the product yield remained below that to be expected from the synthesis results with the reactor of the same design but of a much smaller catalyst bed of 2 l. A closer investigation in this respect disclosed that the large magnitude of temperature rise was mainly due to a high heat transfer resistance across an oil film on the out-side wall of the reactor. For the better performance, therefore, the reactor ought to be modified in construction in order that the heat transfer efficiency across the oil film might be improved. By the use of the reactor which has been improved along this line, the present synthesis experiments are conducted.

The previous paper, in addition, dealt with

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

the calculation of the temperature profile in the catalyst bed on the basis of the concentration gradient determined along the heights of the catalyst bed. Because of the temperature gradient already present in the oil surrounding the reactor, the method of the calculation, however, can be applied with difficulty to the result with the present reactor. In this paper the calculating method with the result is proposed.

Experimental

In an effort to improve the heat transfer efficiency across the oil film on the out-side wall of the previous reactor, the previous reactor system was subjected to some modifications. Fig. 1 shows a schematic diagram of the system after the modifications. The main modification made was that the reactor (A, 10 m. high by 50 mm. I. D.) was placed in a cylinder (B) which was filled with oil (Dowthem) boiling under a reduced nitrogen pressure, whereas the previous reactor had been held in the oil under forced circulation at a fixed flow rate under an atmospheric pressure of nitrogen. A small amount (ca. 200 l./hr.) of nitrogen was always being introduced from a valve (L) into the oil bath by way of a number of openings (0.8 mm. diameter) perforated along two semi-circular tubes placed, opposite to each other, at the bottom of the cylinder. The nitrogen gas passed upwards through the oil, and could easily be controlled at a fixed pressure by means of a leak opened by a magnetic valve (F) which was coupled with a mercury contact manometer (E).

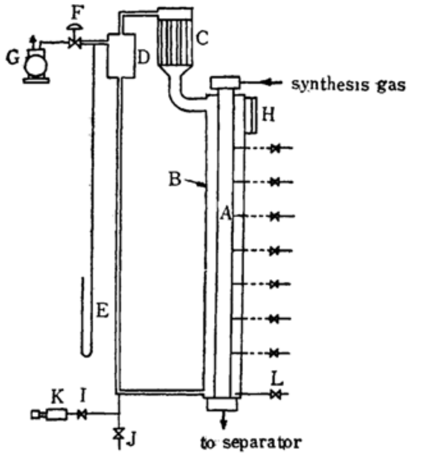

Fig. 1. Schematic diagram of reactor system.
- A, Reactor
- B, Cylinder for oil bath
- C, Condenser
- D, Reservoir
- E, Contact manometer
- F, Magnetic valve
- G, Pump
- H, Level indicator
- I, J, L, Needle valves
- K, Dowtherm feeder

The top zone of the oil bath was equipped with a level indicator (H), by the aid of which the oil was maintained at a constant level by either introducing or withdrawing a small quantity of oil through a valve (I) or (J), respectively. A condenser (C) was placed directly above the top of the cylinder, in which the oil vapor accompanying the nitrogen stream was refluxed back into the oil bath. A reservoir (D) served to avoid a sudden change in the nitrogen pressure. After passing through C, D and F, the gas was finally drawn out by a pump (G).

In view of the kind of reactor type called rectification cooling type, which was originated by Dorschner[2], the present reactor may also be known as such, but it differs from Dorschner's reactor in some respects.

Besides the sintered catalyst (designated catalyst A hereafter) in the previous paper[1], a fused iron catalyst (designated catalyst B hereafter) of the same promoter-composition was employed in this study. Granules of the catalyst ranging from 5 to 2 mm. in size were used, and the catalyst bed of 18.1 l. contained 39.41 kg. of the granules after reduction. The technique of the catalyst pretreatment as well as of the synthesis was essentially the same as was described elsewhere[3] in detail.

Results and Discussion

Results. — Table I shows. together with the synthesis variables, results from a series of five experiments, among which two experiments were carried out by using catalyst A while the other three ones by using catalyst B. Numerals listed in the column of nitrogen pressure serve as a measure to estimate roughly the oil bath temperature: the higher the pressure is, the higher the temperature rises. Further, the axial temperature profiles in the catalyst bed as well as in the oil bath are exemplified in Figs. 2A, B, C and D for experiments Nos. 1, 2, 6 and 7, respectively.

It was after the experiment described in the previous paper[1] (hereafter simply called experiment A) had been made that the bed of catalyst A was used in this study, and hence the bed had already undergone an activity decrease to some extent. In this connection, a much higher yield of the product (oil plus wax) may have not been produced in experiment No. 1 as compared with the yield (14.14 kg./day) in experiment A, in spite of the improvement made for the heat transfer efficiency[4]. Nevertheless, one can yet recognize the effects of the improvement clearly. One of the effects is the axial temperature gradient

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[2] O. Dorschner, *Chem. Ing. Tech.*, **25**, 277 (1953).

[3] M. Kuraishi, H. Ichinokawa et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1588 (1960).

[4] It is to be noted that in experiment No. 1 the temperature at the axial middle point of the oil bath was essentially the same as the oil bath temperature in experiment A.

TABLE I. RESULTS OF SYNTHESIS EXPERIMENTS

Exp.	Catalyst	Pressure kg./cm^2 (gauge)	Nitrogen pressure mmHg	Space velocity of inlet gas hr^{-1}	Space velocity of raw gas hr^{-1}	Volume contraction %	Oil plus wax kg./day	Aqueous product kg./day	Oil plus wax per m^3 (CO+H$_2$) g.	Use ratio H$_2$/CO
No. 1	A	30	580	2250	668	41.1	15.91	21.94	105	1.10
No. 2	A	30	760	2270	816	44.6	21.21	27.45	106	1.11
No. 5	B	25	440	2080	582	41.5	16.83	20.09	131	1.06
No. 6	B	30	520	2125	790	48.1	24.39	32.82	118	1.06
No. 7	B	30	480	1670	785	49.8	26.03	30.96	125	1.10

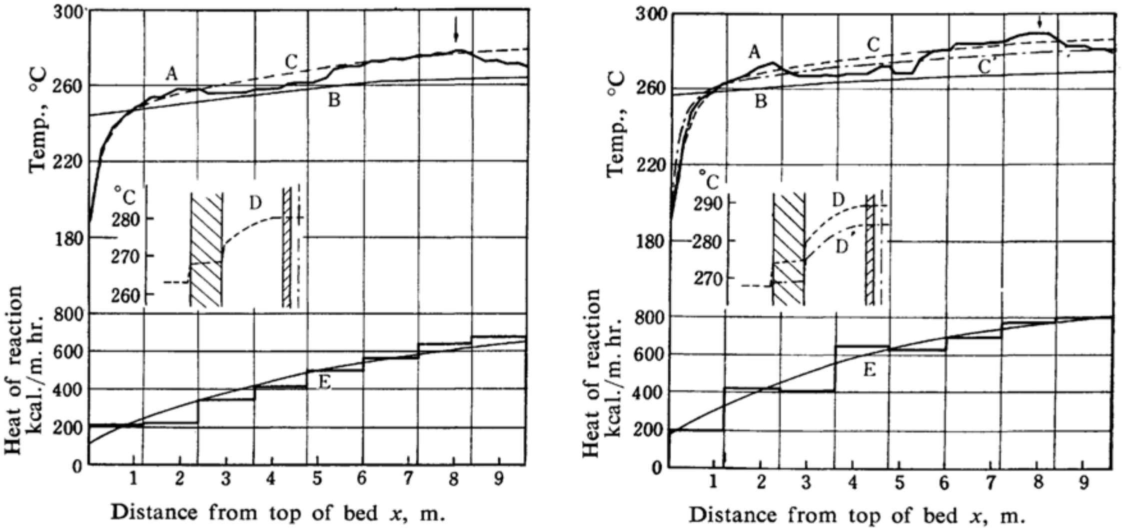

Fig. 2A. Experiment No. 1.

Fig. 2B. Experiment No. 1.
C, D, Temperature profile calculated by the use of $h'_L=600$ kcal./m^2 hr.°C
C′, D′, Temperature profile calculated by the use of $h'_L=4800$ kcal./m^2 hr.°C

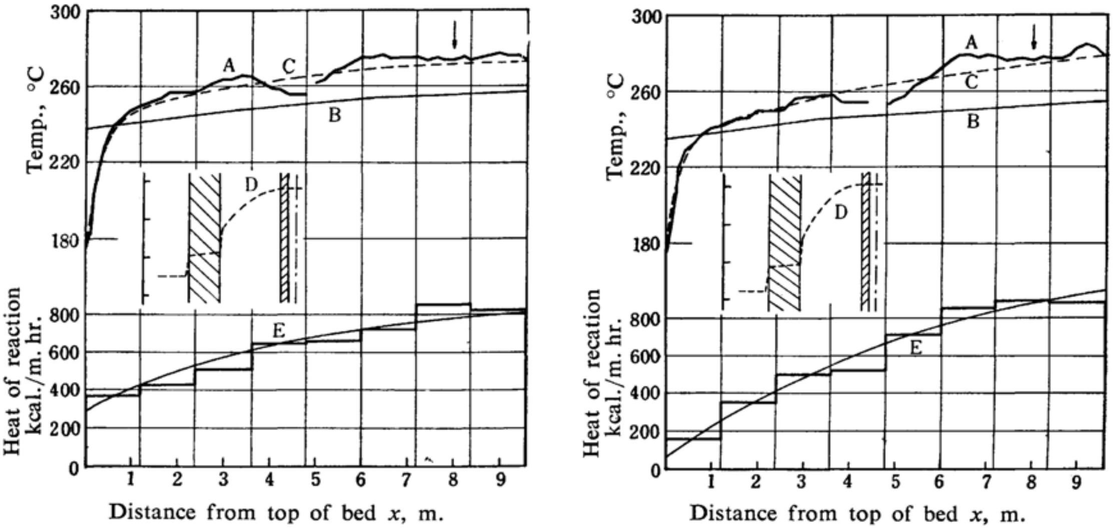

Fig. 2C. Experiment No. 6.

Fig. 2D. Experiment No. 7.

Figs. 2A–D. Experimental and calculated temperature profiles (above) and heat of reaction as function of x (below, E).

A, Experimental temperature profile	B, Oil bath temperature
C, Calculated axial profile	D, Calculated radial profile

in the oil bath, increasing continuously from top to bottom. The appearance of the gradient arises from the fact that the boiling temperature of oil is continuously increased with gravity of increasing amounts of oil in the oil bath cylinder from top to bottom. The temperature gradient thus produced along the oil bath may have helped the catalyst bed temperature to rise with the distance (x) from the top of the bed. In contrast to the above, the temperature profile in the bed of experiment A showed a downward tendency along the lower half of the bed. Another effect is the smaller magnitude of temperature difference between the oil bath and the reactor axis, in other words, the smaller magnitude of the bed over-temperature (hereafter denoted by $(t-t_b)$, where t and t_b are the temperatures measured along the axis of catalyst bed and along the oil bath, respectively), which was 15°C at a maximum for experiment No. 1 while 25°C for experiment A.

By using a fresh bed of catalyst **B** in place of the deteriorated one of catalyst A, much higher yields of the product, attaining from 24 to 26 kg./day, were produced (refer to the results of experiments Nos. 6 and 7), even though the nitrogen pressure was kept below that of experiment Nos. 1 and 2. Moreover, the magnitude of $(t-t_b)$ remained comparatively small: at the region of a maximum $(t-t_b)$, 22 and 30°C for experiments Nos. 6 and 7, respectively. The somewhat larger magnitude of $(t-t_b)$ observed with the latter experiment may be accounted for by a lower space velocity of the inlet gas, details of which will be stated later.

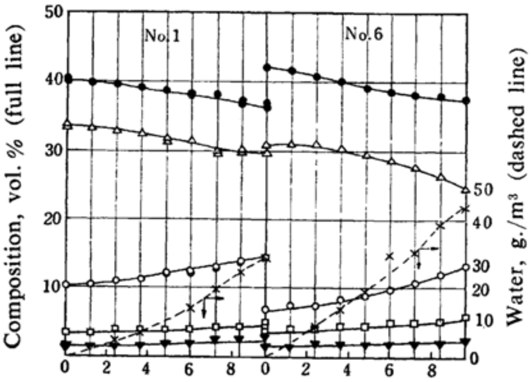

Fig. 3. Concentration gradient along catalyst bed.

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

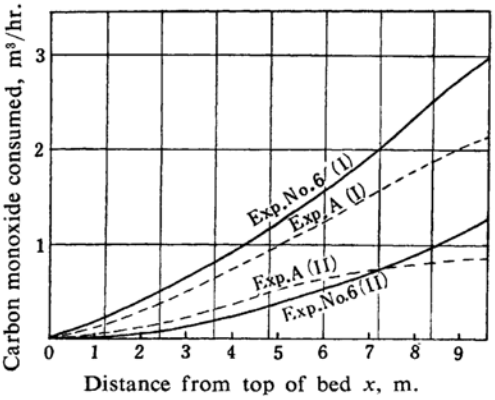

Fig. 4. Carbon monoxide consumed by either reaction (1) or (2) as a function of x.

The concentration gradient of the individual components along the reactor was determined in the same manner that was made in experiment A[1]. Among the results the gradient for experiment No. 6, for instance, is shown in the right half of Fig. 3, while the gradient for experiment A is given again in the other half. Starting with the results of Fig. 3 and following the procedure as reported in the previous paper[1], one can calculate amounts of carbon monoxide consumed with the progress of the synthesis either by $2H_2+CO \rightarrow >CH_2+H_2O$··· (1) or by $CO+H_2O \rightarrow CO_2+H_2$···(2). Fig. 4 illustrates plots of the amount vs. x, together with the recited ones for experiment A. The figure discloses that although the amounts of carbon monoxide consumed by the reaction 1 in the top zone of the catalyst beds differ slightly from each other the amount at the end of the bed in experiment No. 6 attains 3/2.1 times as large as the amount in experiment A. In view of the fact it can be seen that in experiment No. 6 better use was made of the lower half of the catalyst bed than that in experiment A.

Method of Calculating Temperature Profiles in Catalyst Bed.—Because of the presence of the temperature gradient along the oil bath, the solution to the heat balance equation, as cited in the previous paper[1], is to be made under the different boundary conditions from the previous ones. The equation is then given as follows.

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

with the following boundary conditions,

$$t=t_0 \quad \text{at} \quad x=0$$

$$\lambda_r\partial t/\partial r+U(t-t_b)=0 \quad \text{at} \quad r=r_2$$

and $\partial t/\partial r=0$ at $r=r_1$

where C_p is the heat capacity per unit mass of fluid, G is the mass velocity based on an empty tube, r is the distance in lateral direction, λ is the effective thermal conductivity of the catalyst bed system, 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.

A numerical solution of Eq. 1 may be possible. However, the calculation will be very time-consuming since t_b varies with x. As a compromise, it would be rather convenient for the present purpose to start with a more simplified equation of the heat balance, in which the temperature is assumed to be radially uniform at every cross section of the bed that an average temperature[5] (t_{av}) over the bed cross section may simply be taken into account. The solution then gives the axial temperature profile. Once the axial temperature profile has been drawn, Eq. 1 can be solved more easily with respect to a cross section, in the neighborhood of which the axial temperature is kept essentially constant. The solution gives the radial temperature profile.

Under the assumption of uniform temperature across the bed, the following equation of the heat balance can be established,

$$G_pG\mathrm{d}t/\mathrm{d}x+2\pi r_2U'(t-t_b)/S=Q \qquad (2)$$

with the boundary condition that $t=t_0$ at $x=0$. The symbol S in the equation is the cross sectional area of the bed, and the second term in the left-hand side of the equation concerns the heat transfer across the tube wall of the reactor held in the oil bath whose axial temperature gradient is assumed to be given by a linear function of x, namely $t_b=t_{bo}+ax$, where t_{bo} is the oil bath temperature at $x=0$. The constant a takes a value characteristic of the gradient in the oil bath. It should further be noted that U' is to be distinguished from U in Eq. 1. The calculation of U' is made by taking the tube wall coefficient of the heat transfer based on t_{av} (denoted by h') into account whereas U by taking the coefficient based on t at $r=r_2$ (denoted by h) into account. In this paper, h' with respect to the present annular shaped cylinderical bed was evaluated by making use of the formula[6] proposed by Maeda et al.[7] for h' with a cylindrical bed, while h by the aid of the formula[8] by the Hatta et al.[9] In the latter formula, λ_r is taken into consideration.

In Eq. 2, Q is again approximated to

$$Q=C_1\mathrm{e}^{-Mx}-C_2\mathrm{e}^{-Nx} \qquad (3)$$

where C_1, C_2, M and N are constants. Combination of 2 with 3, and subsequent rearrangement give

$$\mathrm{d}t/\mathrm{d}x+A(t-t_{bo}-ax)=G_1\mathrm{e}^{-Mx}-G_2\mathrm{e}^{-Nx} \qquad (4)$$

in which the following abbreviations are introduced.

$$A\equiv2\pi r_2U'/C_pGS,\quad G_1\equiv C_1/C_pG$$
$$G_2\equiv C_2/C_pG \qquad (5)$$

The solution of Eq. 4 is given by

$$t=t_{bo}+\mathrm{e}^{-Ax}\left[t_0-t_{bo}+\frac{G_1}{A-M}\left\{\mathrm{e}^{(A+1)x}-1\right\}-\frac{G_2}{A-M}\left\{\mathrm{e}^{(A-N)x}-1\right\}\right]+a\left\{x-\frac{1}{A}(1-\mathrm{e}^{-Ax})\right\} \qquad (6)$$

On the other hand, under the assumption of $\mathrm{d}t/\mathrm{d}x=0$, Eq. 1 is reduced to a simpler form of

$$\lambda_r\{\mathrm{d}^2t/\mathrm{d}r^2+(1/r)(\mathrm{d}t/\mathrm{d}r\}+Q=0 \qquad (7)$$

with the boundary conditions that $\mathrm{d}t/\mathrm{d}r=0$ at $r=r_1$, and $\lambda_r\mathrm{d}t/\mathrm{d}r+U(t-t_b)=0$ at $r=r_2$. The solution results in Eq. 8.

$$t=t_b+\frac{Qr_2^2}{4\lambda_r}\left[\left\{1-\left(\frac{r}{r_2}\right)^2\right\}+2\left(\frac{r_1}{r_2}\right)^2\ln\frac{r}{r_2}+\frac{2\lambda_r}{Ur_2}\left\{1-\left(\frac{r_1}{r_2}\right)^2\right\}\right] \qquad (8)$$

By the aid of Eqs. 6 and 8 both the axial and the radial temperature profiles can be drawn.

Let us make an approximate check on the accuracy of the present calculation method by performing a profile calculation. The calculation is carried out on the basis of the experimental data of experiment A, and the resulting profiles are shown in Fig. 5 with the dotted and dashed lines, of which the radial one is given for the cross section at $x=6$ m. In the neighborhood of the cross section, the axial temperature has been found nearly constant. For the sake of comparison, the figure is included with the previous profiles (dashed lines) calculated by using the solution with no simplification of Eq. 1. The respective profiles calculated by either one of the two

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[5] The average temperature (t_{av}) is defined by

$$t_{av}=\int_{r_1}^{r_2}t\cdot2\pi r\mathrm{d}r/\pi(r_2^2-r_1^2)$$

[6] $h'D/k=4.90(R_{ep})^{0.60}\mathrm{e}^{\cdot-2.2d_p/D}$, where D is the diameter of bed, k is the thermal conductivity of fluid, R_{ep} is the modified Reynolds number, and d_p is the diameter of catalyst granules (4 and 3.4 mm. for catalysts A and B, respectively). In the evaluation of h', D_{eq} defined by $D_{eq}=D_2-D_1$ is used in place of D.

[7] S. Maeda and K. Kawazoe, *Chem. Eng. Japan* (*Kagaku Kogaku*), **17**, 276 (1953).

[8] $\lambda_r/k=0.209(R_{ep})^{0.87}$ and $hD_{eq}/\lambda_r=127(R_{ep}\cdot d_p/D_{eq})^{-0.87}$.

[9] S. Hatta and S. Maeda, *Chem. Eng. Japan* (*Kagaku Kikai*), **13**, 79 (1949).

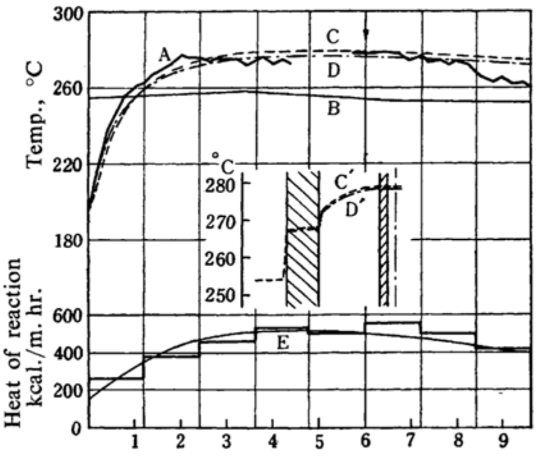

Fig. 5. Experimental and calculated temperature profiles (above) and reaction heat as a function of x (below, E) for experiment A.

A, Experimental temperature profile
B, Oil bath temperature
C, C′, Profiles as cited in previous paper
D, D′, Profiles calculated by the aid of Eqs. 6 and 8

different methods show a good approximation with each other. However, it should be noted that the present method of calculating the axial temperature profile is available only when λ is so high that the radial temperature gradient can be ignored. It otherwise may lead to errors, for instance, in such a case that the synthesis is made by the once-through operation where the mass velocity of the inlet gas, as a consequence, λ is usually much lower.

Calculation of Temperature Profile. — Before proceeding to the profile calculation, the coefficient (h_L) of heat transfer referred to the out-side wall of present reactor, over which the oil film is kept under nucleated boiling, has to be evaluated. Although there have appeared a few papers[10] dealing with the heat transfer phenomenon considered, none of them except for the paper by Nishikawa[11] is available for the calculation. Accordingly, a rough estimation of h_L is made for experiment No. 2 by means of Nishikawa's formula, which results in the value of 4800 kcal./m^2 hr. °C. By using this value the profile calculation is made[12]. The profiles thus drawn are shown in Fig. 2B with the dotted and dashed lines, which appear to be in a poor agreement with the experimental profiles: the calculated axial temperature profile rises more rapidly in the top zone while it lies below the experimental one in the lower half of the catalyst bed, and in addition the radial temperature profile at the cross section of $x=8$ m. shows a maximum temperature across the bed of 284.3°C, in contrast to the measured one of 289°C. The disagreement may probably be due to too high an estimated value of h'_L, consequently of U'.

The calculation is then repeated with other different values of h'_L for a better agreement between the measured axis-temperature in the bed and the calculated one, and finally $h'_L=600$ kcal./m^2 hr. °C, consequently $U'=391$ kcal./m^2 hr. °C, is conveniently chosen, by the choice of which the temperature of 289.5°C is attained. The value of h'_L has thus appeared only one eighth of the value afore-cited[13], but it is still 3.5 times as much as the value in the previous reactor. The axial profile calculations have then been made, and an improvement in the accordance between the calculated and the measured profiles is obtained (refer to the dashed line in Fig. 2B). The same calculations made on the basis of the data of the other experiments of Nos, 1, 6 and 7 results in the profiles as cited in Figs. 2A, C and D, respectively. The profiles are in a good agreement with measured ones, except for a small intermediate range where the measured profile lies somewhat below the calculated one. Moreover, the radial temperature profile is visualized by the calculation as shown in the figure, and a comparison of the profile with that in Fig. 5 is suggestive of the improving effect of the present procedure on the heat transfer efficiency across the out-side wall. In this study, however, no experimental evidence is available for the radial profile.

It should be noted that the present procedure of improving the heat transfer efficiency can effectively be applied only when the difficulty exists in the heat transfer resistance across the liquid film on the out-side wall of the reactor. In this respect, a comparison between the results of experiment Nos. 6 and 7 shows that the magnitude of $(t-t_b)$ is a

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[10] Y. Y. Hsu and J. W. Westwater, *Am. Inst. Chem. Engrs. J.*, **4**, 58 (1958); C. Corty and A. S. Foust, *Chem. Eng, Progr.*, *Symposium Ser.* No. 17, **51**, 1 (1955). S. A. Guerrieri and R. D. Talty, ibid., No. 18, **52**, 69 (1956), et al.

[11] K. Nishikawa, *Trans. Jap. Soc. Mech. Eng.*, No. 120, **22**, 551 (1956).

[12] In fact, the temperature gradient in the oil bath is convex upwards instead of being a linear function of x, as shown in Figs. 2A, D. In the calculation of the profile, a few axial step lengths are chosen, and the solution is applied to each of the steps successively. Although the integration constant in the solution remains the same in the first step where the boundary condition is $t=t_0$ at $x=0$, it differs in value for the succeeding steps because the different boundary condition that t at the end of the first step is equal to t at the top of the second step, and so forth, are established.

[13] We are not as yet certain of the accurate reason why the value of h'_L thus chosen is far smaller than that obtainable from Nishikawa's formula.

little smaller for experiment No. 6 which was conducted under the essentially same operating conditions, except for the greater G, than those in experiment No. 7. As regards the present two experiments where h'_L is as high as 600 kcal./m^2 hr. °C, the greater value of λ[14], which is necessarily accompanied by the increasing G, may therefore become rather responsible for the smaller magnitude of $(t-t_b)$. The effect of varying values of G on $(t-t_b)$ can be seen more clearly when the results of the once-through operation is considered[15].

Dorschner[2] has already pointed out that the outside wall temperature gradient increasing from top to bottom exerts an advantageous effect on an efficient use of the catalyst bed. For the purpose of producing such a temperature gradient, he employed a bath of an oil mixture consisting of hydrocarbons of different boiling points, whereas in the present procedure one kind of oil, Dowtherm, is simply used. In addition, the procedure has another advantage of providing a better means of temperature control: the oil bath temperature has to be increased successively to follow the deterioration of the catalyst activity, which can be done by a simple regulation of the nitrogen pressure. However, it suffered from the following limitation that a considerable magnitude of the temperature difference (for example, ca. 20°C from top to bottom in the present reactor) can not be produced until the reactor reaches as high as 10 m.

Summary

The present experiments on the Fischer-Tropsch synthesis have been made with the reactor which was placed in a bath of oil boiling under a reduced nitrogen pressure. The heat transfer efficiency referred to the out-side wall of the reactor has been improved considerably, and, as a consequence, the magnitude of the bed over-temperature remains comparatively small, in spite of the high yield of the product attaining 24~26 kg./day.

The axial and the radial temperature profiles have been separately calculated on the basis of the concentration gradient determined along the heights of the reactor: first the calculation of the former profile under the assumption of uniform temperature across the bed, and secondly that of the latter profile at a cross section in the neighborhood of which the axial temperature is approximately constant. By the convenient choice of 600 kcal./m^2 hr. °C for the tube wall coefficient of heat transfer referred to the out-side wall of the present reactor, the calculated axial temperature profile is in good agreement with the experimental profile except for a small intermediate range.

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[14] The values of λ for experiment Nos. 6 and 7 were 5.09 and 4.03 kcal./m.·hr. °C, respectively.

[15] The results will be reported elsewhere.