



# HOKKAIDO UNIVERSITY

Title	Effects of Design and Operation Variables on the Autothermic Reactor
Author(s)	KASHIKI, Isamu; 櫻木, 勇; MIKI, Masayuki et al.
Citation	北海道大學水産學部研究彙報, 31(3), 265-275
Issue Date	1980-08
Doc URL	<a href="https://hdl.handle.net/2115/23726">https://hdl.handle.net/2115/23726</a>
Type	departmental bulletin paper
File Information	31(3)_P265-275.pdf





5. Constant specific heat of reacting mass as a whole, irrespective of the composition and temperature.
6. Unimolecular reaction  $A \xrightleftharpoons[k_{-1}]{k_1} B$ ,  $k_1/k_{-1}=K$  occurring, with the heat of reaction,  $\Delta H$  and the energy of activation,  $E$ .
7. Overall heat transfer coefficient proportional to the 0.75th power of the mass velocity.
8. Constant temperature of the inlet reactant ( $\theta_0=\text{constant}$ ).

Under these assumptions, following nine simultaneous equations should hold for the 3-pass mixed-flow reactor, and, if  $\beta_2$  vanishes, and hence  $\theta_2$  equals  $\theta_3$ , they represent the two-pass counter-flow reactor.

$$\theta_2 = [\gamma / \{b + \gamma/2(1-b)\}] \cdot \theta_7 \quad (1)$$

$$\theta_6 = \theta_7 + b\theta_2 \quad (= \Delta X + \theta_0 + b\theta_2) \quad (2)$$

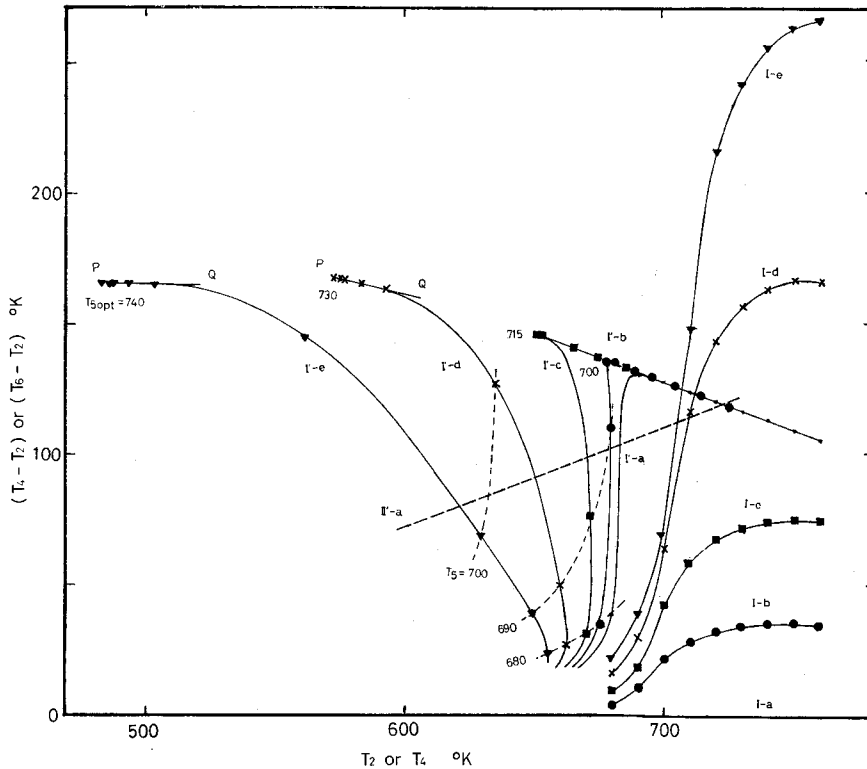


Fig. 2. Effect of heat transfer between the catalyst bed and the cooling pipes. ( $F=920$ ,  $C_0C_p=47.2$ ,  $C_0=4.44$ ,  $C_i=4.20$ ,  $l=5$ ,  $a=b=1$ ,  $\Delta H=-7000$ ,  $E=40000$ ,  $k_0=0.5 \cdot 10^{14}$ ,  $K_0=0.4735 \cdot 10^{-2}$ ) Curved line I refers to the relation between  $T_4$  and  $(T_4 - T_2)$ ,  $I'$ , to the relation  $T_2$  and  $(T_6 - T_2)$  from Eqs. (6), (7), (8), whereas straight line II' denotes the relation between  $T_2$  and  $(T_6 - T_2)$  from Eqs. (1), (2).  $U_1S_1=0$  for I-a, I'-a; =2875 for I-b, I'-b; =5750 for I-c, I'-c; =11500 for I-d, I'-d; =17250 for I-e, I'-e.

$$\theta_5 = ab\theta_4 + (1-a)b\theta_2 + \theta_Q \quad (3)$$

$$X - X_i = ab(\theta_Z - \theta_Y) + \theta_X - b\theta_2 - \theta_Q \quad (4)$$

$$\Delta X = X_f - X_i = \theta_7 - \theta_Q \quad (5)$$

$$\frac{d\theta_X}{d\lambda} = V' - \beta_1(\theta_X - \theta_Y) - \beta_2(\theta_X - \theta_Z) \quad (6)$$

$$\frac{d\theta_Y}{d\lambda} = \frac{\beta_1}{ab}(\theta_X - \theta_Y) \quad (7)$$

$$\frac{d\theta_Z}{d\lambda} = \frac{\beta_2}{ab}(\theta_X - \theta_Z) \quad (8)$$

$$V' = \exp\{-\varepsilon/(\theta_0 + \theta_X)\} (1 - X - X/[K_0 \exp\{\delta/(\theta_0 + \theta_X)\}]) \quad (9)$$

where  $V' = V/k_0C_0$

and the boundary conditions for (6), (7) and (8) are

$$\lambda = 0; \theta_X = \theta_5, \theta_Y = \theta_4, \theta_Z = \theta_2$$

$$\lambda = \lambda_0; \theta_X = \theta_6, \theta_Y = \theta_Z = \theta_3$$

The method of solution has been given in the previous paper.

### The Result and Discussion

#### *Effect of Heat Transfer between the Catalyst Bed and the Cooling Tubes in the Internal Heat Exchanger*

The parameters,  $S_1$  and  $S_2$  are design variables, but  $U_1$  and  $U_2$  depend upon flow rates and so not fundamental variables.  $U_1S_1$  and  $U_2S_2$  represent heat transfer capacity and affect  $\beta_1$  and  $\beta_2$  but do not affect  $\gamma$ . Fig. 2 shows the effect of  $U_1S_1$  on the performance of the 2-pass counter-flow autothermic reactor, from which it can be seen that:

(1) If there is no heat transfer, in which case the reactor reduces to an adiabatic one, the reactor has no unstable zone as proposed by van Heerden<sup>3</sup>, because the slope of any tangent to the curved line I'-a is at least not less than null. However, in the presence of the

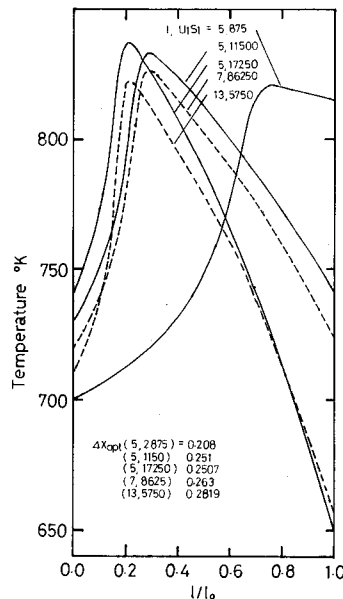


Fig. 3. Optimum temperature profiles of the catalyst bed at different catalyst bed lengths and at different degrees of heat transfer in the autothermic part.

( $C_0C_p=47.2$ ,  $C_0=4.44$ ,  $C_i=4.20$ ,  $a=b=1$ ,  $\Delta H=-7000$ ,  $E=40000$ ,  $k_0=0.5 \cdot 10^{-4}$ ,  $K_0=0.4735 \cdot 10^{-2}$ )

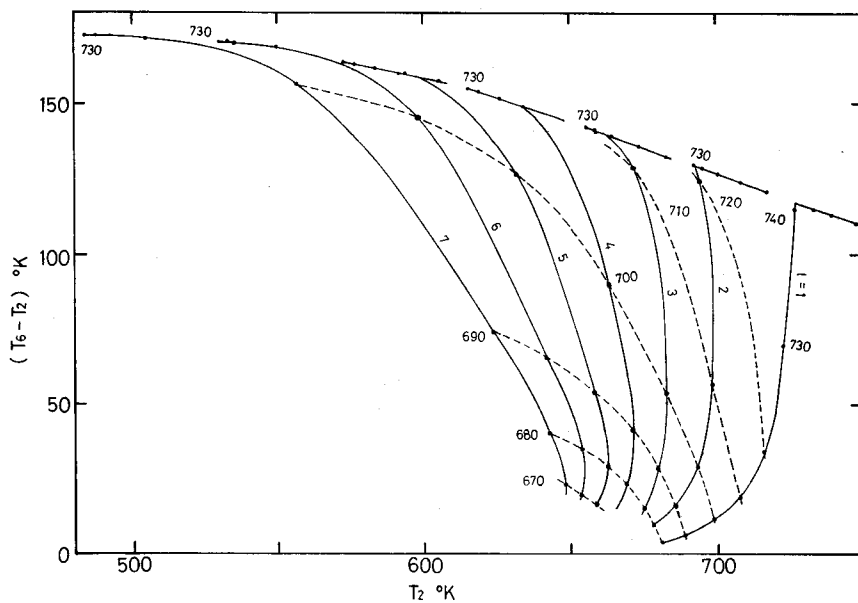


Fig. 4. Effect of catalyst bed length. ( $F=920$ ,  $C_0C_p=47.2$ ,  $C_0=4.44$ ,  $C_i=4.20$ ,  $U_1S_1=11500$ ,  $a=b=1$ ,  $\Delta H=-7000$ ,  $E=40000$ ,  $k_0=0.5 \cdot 10^{-2}$ ,  $K_0=0.4735 \cdot 10^{-2}$  Catalyst bed length; 1, 2, 3, 4, 5, 6, 7.

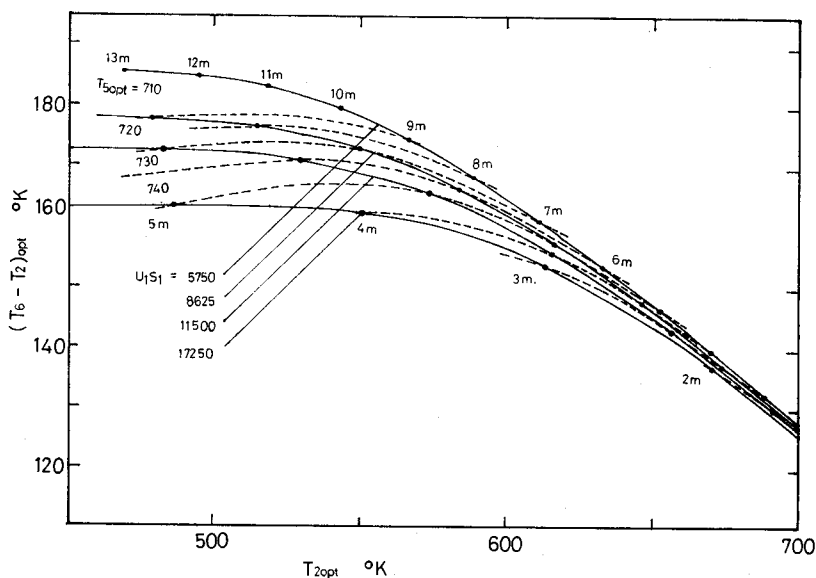


Fig. 5. Effect of catalyst bed length at different  $U_1S_1$ 's. (The condition is the same as in Fig. 4 except for the values of  $U_1S_1$ 's, which take the values of 5750, 8675, 11500, 17250.) Catalyst bed length; 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13.

external heat exchanger, the unstable zone based on our criterion does exist, as can be seen from the relation between the curved line I'-a and the straight line II'-a<sup>1</sup>).

(2) With the presence of the heat transfer, the van Heerden unstable zone appears, and as the heat transfer increases, both van Heerden and our unstable zones increase, the curve I' which expresses the solution of Eqs. (6), (7) and (8) on the  $T_2-(T_c-T_2)$  plane takes a sigmoidal shape whose upper left part projects sharper,  $T_2$  falls,  $T_{5opt}$  rises, and the slope of the curved line at the upper stable zone,  $PQ$ , tends to null.

(3) Provided that the catalyst bed length is held constant, a condition which gives maximum  $\Delta X_{opt}$  exists at some  $U_1S_1$  value.

The optimum temperature profiles of the catalyst bed at different  $U_1S_1$ 's are depicted in Fig. 3.

*Effect of Catalyst Bed Length*

The catalyst bed length,  $l_0$ , is a design variable and affects only  $\lambda_0$  and does

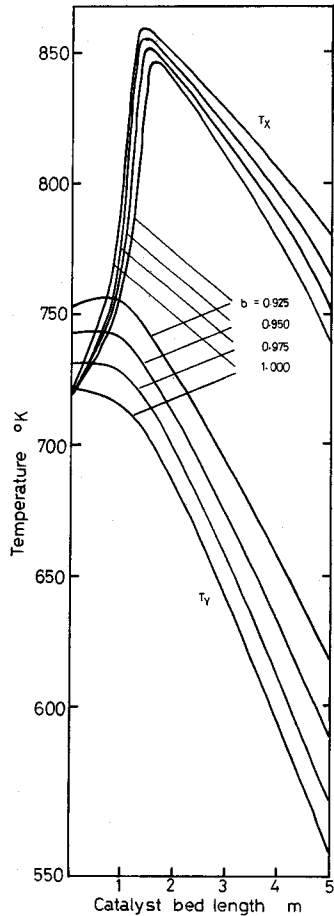


Fig. 6. Temperature profiles of the catalyst bed with or without bypass ( $b$ ). ( $F=920, C_oC_p=47.2, C_o=4.44, C_i=4.20, U_1S_1=11500, a=1, l=5, \Delta H=-7000, E=14000, k_o=0.5 \cdot 10^{14}, K_o=0.4735 \cdot 10^{-2}$ )  $b=1.000, 0.975, 0.950, 0.925$ .

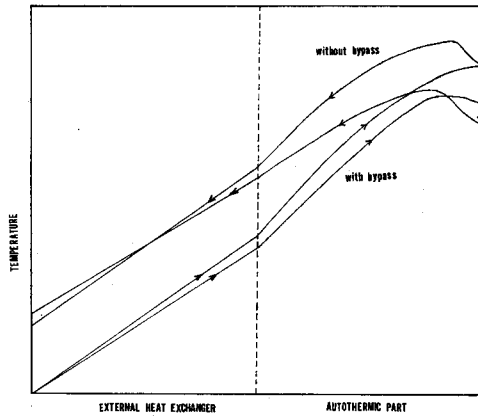


Fig. 7. Temperature profile of the whole reactor when the bypass ( $b$ ) is used. Left half refers to the external heat exchanger and right half, the catalyst bed.

Fig. 6. Temperature profiles of the catalyst bed with or without bypass ( $b$ ). ( $F=920, C_oC_p=47.2, C_o=4.44, C_i=4.20, U_1S_1=11500, a=1, l=5, \Delta H=-7000, E=14000, k_o=0.5 \cdot 10^{14}, K_o=0.4735 \cdot 10^{-2}$ )  $b=1.000, 0.975, 0.950, 0.925$ .

not affect  $\beta_1$  and  $\gamma$ . The effect of increased catalyst bed length at constant  $U_1S_1$ , is somewhat similar to the effect of increased heat transfer at constant catalyst bed length. The differences are that the conversion increases at a decelerating rate and no maximum  $\Delta X_{opt}$  exists, and  $T_{5opt}$  falls, with an increased bed length (Fig. 4). As can be seen from Fig. 5,  $(U_1S_1)_{opt}$  which gives maximum  $\Delta X_{opt}$ , or  $(T_2 - T_6)_{opt}$ , at the constant catalyst bed length, decreases with the increase in catalyst bed length. In short, the effect of prolonged catalyst bed length is to increase conversion while keeping lower catalyst temperature. The optimum catalyst temperature at different bed lengths are shown in Fig. 3.

In the commercial reactor, longer catalyst bed implies more catalyst volume, more heat loss to the surroundings and longer equipment, and hence more capital investment, whereas less heat transfer between the catalyst bed and the internal heat exchanger brings about less capital investment. The cost of the reactor is said commonly to be only about ten percent of the total capital cost summed up within battery limit, while the more catalyst volume and the lower catalyst temperature mean usually safer operation and longer catalyst life. The decision upon

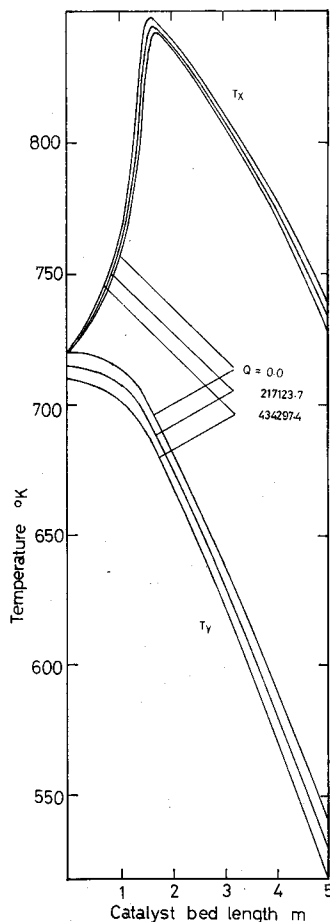


Fig. 8. Temperature profiles of the catalyst bed with or without heater. ( $F=920$ ,  $C_0C_p=47.2$ ,  $C_0=4.44$ ,  $C_i=4.20$ ,  $U_1S_1=11500$ ,  $l=5$ ,  $a=b=1$ ,  $\Delta H=-7000$ ,  $E=40000$ ,  $k_0=0.5 \cdot 10^{14}$ ,  $K_0=0.4735 \cdot 10^{-2}$ )  $Q=0$ , 217123.7, 434297.4.

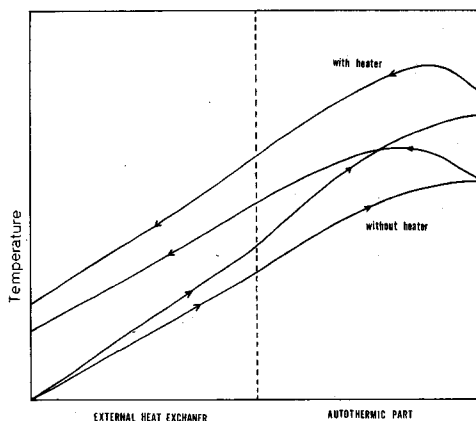


Fig. 9. Temperature profile of the whole reactor when the heater is used. Left half refers to the external heat exchanger and right half, the catalyst bed.

the catalyst bed length depends upon their compromise which places usually more emphasis on conversion, safety and life of catalyst.

### Effect of Bypass and Heater

As can be seen from the mathematical model, the bypass (*b*) connecting the input reactant line to the catalyst bed inlet and the heater mounted at the catalyst bed inlet affect the behavior of the autothermic part and the external heat exchanger through the operation variable, *b* and  $\theta_2$ . Fig. 6 which depicts the temperature profiles of the catalyst beds with or without a bypass, discloses characteristic features of interest that, with a bypass,  $T_4$  is higher than  $T_5$ , and the curve representing  $T_Z$  has a maximum at the intersection of the lines expressing  $T_X$  and  $T_Y$ . In Fig. 7 which pictures the temperature profile of the whole reactor,  $T_2$ ,  $T_4$ ,  $T_5$ ,  $T_6$  and the whole temperature profile tend to fall, with decreasing *b*, and, because the bypass is always used for adjusting the temperature distribution, the conversion,  $\Delta X$ , increases.

By contrast, in Fig. 8 which displays the temperature profiles with or without a heater, it is seen that, with a heater,  $T_5$  is higher than  $T_4$  and the curve representing  $T_Y$  has positive slope and no maximum at any place, and, as can be seen from Fig. 9,  $T_2$ ,  $T_4$ ,  $T_5$ ,  $T_6$  and the whole catalyst temperature rise, with increased heating, and the conversion,  $\Delta X$ , increases as a result of adjusted temperature distribution.

Another bypass (*a*) connecting the exit of the reactant from the external heat exchanger to the inlet of the catalyst bed (Fig. 1), unlike the bypass (*b*), does not alter the reactant throughput in the external heat exchanger. Its function is much like the bypass (*b*) except less effective and less frequently used, and therefore not dealt with in this paper.

### Effect of Feed Rate

Like the bypass (*b*) and the heater, feed rate or throughput is also an operation variable and affects the performance of the external heat exchanger and the autothermic part through changing the values of  $\gamma$ ,  $\lambda_0$ , and further,  $\beta_i$ , because  $U_i$  depends on *F*. Fig. 10 shows that increased feed rates at constant  $T_5$ , always induce levelling off of the temperature profiles, while Fig. 11 discloses an interesting

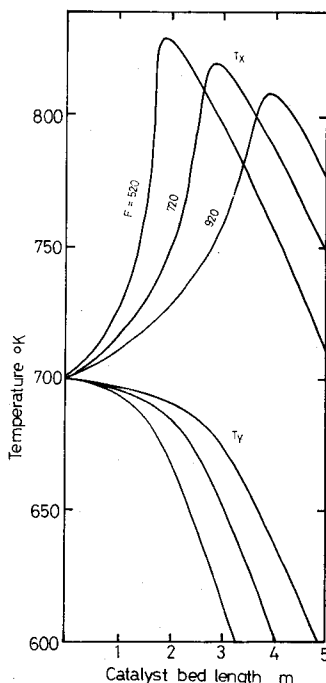


Fig. 10. Temperature profiles of the catalyst bed having the same  $T_5$  at different flow rates. ( $C_0 C_p = 47.2$ ,  $C_0 = 4.44$ ,  $C_i = 4.20$ ,  $U_1 S_1 = 6.0 \cdot F^{0.75} \cdot 11.5$ ,  $a = b = 1$ ,  $l = 5$ ,  $\Delta H = -7000$ ,  $E = 40000$ ,  $k_0 = 0.5 \cdot 10^{14}$ ,  $K_0 = 0.4735 \cdot 10^{-2}$ )  $F = 520, 720, 920$ .

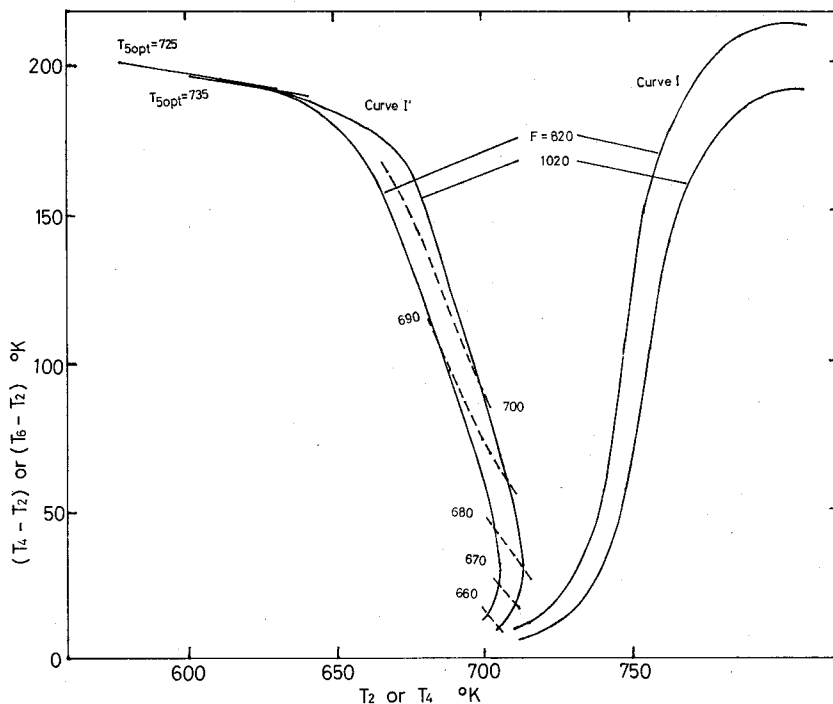


Fig. 11. Effect of flow rate. ( $C_0 C_p = 47.2$ ,  $C_0 = 4.44$ ,  $C_i = 4.44$ ,  $U_1 S_1 = 6.0 \cdot F^{0.75} \cdot 11.5$ ,  $a = b = 1$ ,  $l = 5$ ,  $\Delta H = -7000$ ,  $E = 40000$ ,  $k_0 = 0.5 \cdot 10^{14}$ ,  $K_0 = 0.4735 \cdot 10^{-2}$ )  $F = 820, 1020$ .

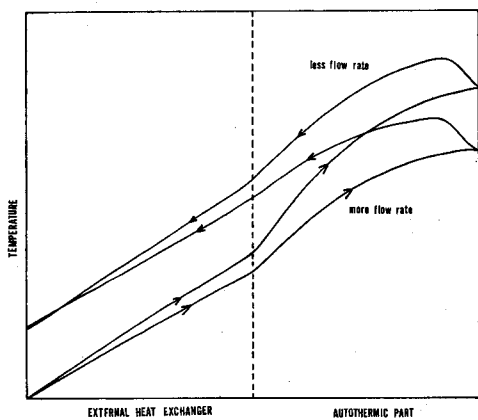


Fig. 12. Temperature profile of the whole reactor at different flow rates. Left half refers to the external heat exchanger and right half, the catalyst bed.

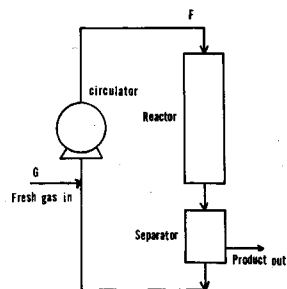


Fig. 13. Flow chart of the synthesis loop applied to the manufactures of ammonia and methanol.

fact that all the curves representing the relation between  $T_2$  and  $(T_6 - T_2)$  or  $\Delta X$ , pass practically the same line at the upper stable zone, irrespective of feed rate. If the effect of feed rate on the external heat exchanger is taken into consideration, the temperature profiles of the whole reactor at different feed rates can be depicted schematically as shown in Fig. 12. Thus the increase in feed rate implies invariable approach to instability notwithstanding slight increases in conversion, and this explains the so-called "blow out", or sudden drop of catalyst temperature which occurs when too much feed is supplied.

### Role of Pressure

We have assumed, up to this point,  $C_0$ , and accordingly, the reaction pressure is constant, which is, of course, not the real situation. There are two important cases in the application of the autothermic reactor which deserve special attention regarding the role of pressure, of the syntheses of ammonia and methanol, their characteristic flow chart, in common, being shown in Fig. 13.

When the catalyst is new and its activity is high, the reaction progresses rapidly, and much product is produced and taken out from the reaction loop, therefore, provided that the reactant feed rate to the loop,  $G$ , is held constant, the pressure tends to fall. However, a lowered pressure gives rise to a decrease in the reactor performance, through lowered circulator capacity,  $FC_0$ , which is proportional to the pressure, and through slow-down of the reaction velocity which is proportional to  $C_0$ . Thus there appears a new steady condition, as a result of their compromise, at a lower pressure.

It is interesting to note that, in theory, another steady condition can be thought of without lowering the pressure, by raising the catalyst temperature and thereby bringing about slow-down of the reaction velocity, and still other innumerable steady conditions, by combining pressure lowering and temperature raising, which, in practice, never occur spontaneously because of less mechanical and thermodynamical stabilities.

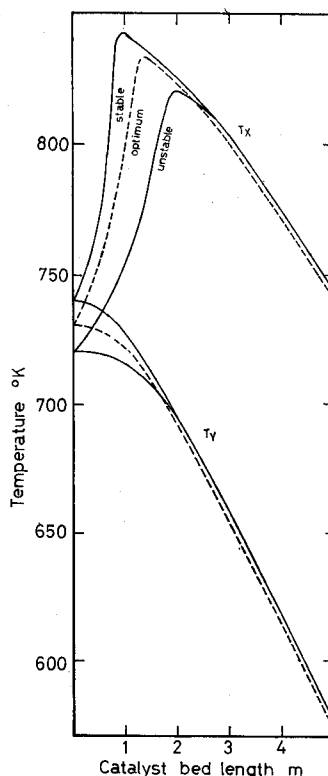


Fig. 14. Temperature profiles of the catalyst bed near optimum conversion. ( $F=920$ ,  $C_0C_p=47.2$ ,  $C_0=4.44$ ,  $C_i=4.20$ ,  $U_1S_1=11500$ ,  $l=5$ ,  $a=b=1$ ,  $\Delta H=-7000$ ,  $E=40000$ ,  $k_0=0.5 \cdot 10^{14}$ ,  $K_0=0.4735 \cdot 10^{-2}$ ) The dashed line shows the one at the optimum condition. The upper solid line refers to a stable condition, whereas the lower one, an unstable condition.

Mathematically, in the simultaneous equations, (1) through (9),  $C_0$  is proportional to pressure, and, by assumption,  $U_1$ ,  $U_2$  and  $U_X$  are proportional to the 0.75th power of  $C_0$ , so that  $\beta_1$ ,  $\beta_2$  and  $\gamma$  are inversely proportional to the 0.25th power of pressure, and their increase due to the lowered pressure induces  $\theta_2$ ,  $\theta_3$ ,  $\theta_4$ ,  $\theta_5$ ,  $\theta_6$  and the whole catalyst temperature profile to rise, and consequently, the conversion,  $\Delta X$ , and the space time yield,  $FC_0\Delta X$  to decrease.

As the catalyst deteriorates, the pressure gradually increases and finally reaches the prescribed value, and the flow rate must be reduced thereafter until shut-down.

#### *Catalyst Temperature Profile near Optimum Conversion*

In Fig. 14, the upper solid curve refers to a stable condition, and the lower, for an unstable condition. They are nearly the same except at the upstream part, which suggests that they are differentiable most sharply by measuring the temperature there. Besides, this portion senses possible disturbances earliest. This explains the reason why it is used primarily as a measuring point for automation.

#### Nomenclature

- $A$ : Reactant
- $a$ : Fraction of the reactant which enters the internal heat exchanger to that which leaves the external heat exchanger
- $B$ : Product
- $b$ : Fraction of the reactant which passes through the external heat exchanger to total input reactant
- $C_0$ : Concentration or density of the input and the reacting mass at any position, in kg-mol/m<sup>3</sup>
- $C_i$ : Concentration of the product in the input, in kg-mol/m<sup>3</sup>
- $C_f$ : Concentration of the product in the output, in kg-mol/m<sup>3</sup>
- $C_p$ : Specific heat of reactant (and also, product), in kcal/mol, °C
- $E$ : Energy of activation, in kcal/kg-mol
- $F$ : Flow rate per unit catalyst cross-sectional area perpendicular to the flow direction, in m<sup>3</sup>/m<sup>2</sup>, h
- $G$ : Flow rate per unit catalyst cross-sectional area of the input to the synthesis loop, in m<sup>3</sup>/m<sup>2</sup>, h
- $\Delta H$ : Heat of reaction assumed positive for an endothermic reaction, in kcal-kg/mol
- $K_0$ : Apparent equilibrium constant at 0°K
- $k_0$ : Preexponential factor of the unimolecular rate constant, in h<sup>-1</sup>
- $l$ : Distance measured from the inlet of the catalyst bed along the flow, in m
- $Q$ : Heat input from the surroundings per unit catalyst cross-sectional area per unit time at the inlet of the catalyst bed, in kcal/m<sup>2</sup>, h
- $R$ : Gas constant
- $S$ : Heat transfer area per unit cross-sectional area and per unit length of the catalyst bed, in m<sup>2</sup>/m<sup>3</sup>
- $S_1$ :  $S$  between the catalyst bed and the cooling pipe in the counter-flow internal heat exchanger, in m<sup>2</sup>/m<sup>3</sup>
- $S_2$ :  $S$  between the catalyst bed and the cooling pipe in the parallel-flow

- internal heat exchanger, in  $\text{m}^2/\text{m}^3$
- $S_X$ : Heat transfer area of the external heat exchanger per unit cross-sectional area of the catalyst bed, in  $\text{m}^2/\text{m}^2$
- $T_i$ : Temperature at point  $i$  or realm  $i$ , in  $^\circ\text{K}$
- $U_1$ : Overall heat transfer coefficient between the catalyst bed and the counter-flow cooling pipe in the internal heat exchanger, in  $\text{kcal}/\text{m}^2, \text{h}, ^\circ\text{K}$
- $U_2$ : Overall heat transfer coefficient between the catalyst bed and the parallel-flow cooling pipe in the internal heat exchanger, in  $\text{kcal}/\text{m}^2, \text{h}, ^\circ\text{K}$
- $U_X$ : Overall heat transfer coefficient at the external heat exchanger, in  $\text{kcal}/\text{m}^2, \text{h}, ^\circ\text{K}$
- $V$ : Unimolecular reaction rate, in  $\text{kg}\text{-mol}/\text{m}^3, \text{h}$
- $V'$ : Dimensionless unimolecular reaction rate,  $V/k_0C_0$
- $X_i$ : Mole fraction of the product at the reactor inlet,  $C_i/C_0$
- $X_f$ : Mole fraction of the product at the reactor outlet,  $C_f/C_0$
- $\Delta X$ : Conversion,  $X_f - X_i$
- $\beta_i$ : Dimensionless heat transfer coefficient,  $U_i S_i / (k_0 C_0 C_p)$
- $\gamma$ : Dimensionless heat transfer coefficient,  $U_x S_x / (FC_0 C_p)$
- $\delta$ : Constant,  $C_p/R$
- $\varepsilon$ : Constant,  $C_p E / R(-\Delta H)$
- $\lambda$ : Dimensionless catalyst bed length,  $k_0 l / F$
- $\theta_i$ : Dimensionless temperature assuming  $T_1=0$ ,  $C_p(T_i - T_1) / (-\Delta H)$
- $\theta_0$ : Absolute dimensionless temperature corresponding to  $T_1$ ,  $C_p T_1 / (-\Delta H)$
- $\theta_Q$ : Dimensionless temperature rise due to the heating from outside,  $Q / FC_0 C_p$

Subscript opt refers to the condition which gives maximum conversion among the solutions of Eqs. (6), (7) and (8) (point P in Fig. 2).

### References

- 1) Kashiki, I, Miki, M., Suzuki, A. and Sakai, M. (1979). Analysis of autothermic reactors with external heat exchangers. *Bull. Fac. Fish. Hokkaido Univ.* **30**(4), 323-332.
- 2) Baddour, R.F., Brian, P.L.T., Logeais, B.A. and Eymery, J.P. (1965). Steady-state simulation of an ammonia synthesis converter. *Chem. Eng. Sci.* **20**, 281-292.
- 3) van Heerden, C. (1953). Autothermic process, properties and reactor design. *Ind. Eng. Chem.* **45**, 1242-1247.