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Title	Analysis of Autothermic Reactors
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Citation	, 30(4), 323-332
Issue Date	1979-11
Doc URL	http://hdl.handle.net/2115/23702
Type	bulletin (article)
File Information	30(4)_P323-332.pdf

Instructions for use

Analysis of Autothermic Reactors

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Abstract

Autothermic reactors equiped with external heat exchangers – two 2-pass reactors (counter-flow and parallel-flow) and two 3-pass reactors (double-pipe and mixed-flow) — are simulated and discussed from viewpoints of stability and optimization.

The 3-pass double-pipe reactor gives maximum conversion when the heat transfer between the inner and the outer pipes vanishes, so it had better be classified as a 2-pass parallel-flow reactor.

With the presence of an external heat exchanger, the stability criterion thus far presented for the autothermic reactor becomes insufficient, and another criterion bases on the relation between the autothermic part and the external heat exchanger which embraces the above criterion should be used.

The 3-pass mixed-flow reactor includes the the two 2-pass reactors as its extreme cases, and can give maximum conversion of the three.

The temperature profile spreads narrowest for the parallel-flow reactor, wider for the counter-flow reactor and the 3-pass reactor, whereas that for the 3-pass reactor is variable.

Introduction

By an autothermic reactor, that type of catalytic reactors used for exothermic reactions which has heat exchanger(s) within its catalyst bed through which the reactant flows to preheat itself and, at the same time, to level off the temperature profile of the bed, is meant. It is commonly used along with an external heat exchanger which functions to raise the input reactant to a high enough temperature to start the reaction (Figs. 1).

There have been many reports and discussions on autothermic reactors[1,2], but none have ever referred to the relationship between the autothermic part and the external heat exchanger notwithstanding they build up a so-called "recycle set" whose mathematical model must be solved simultaneously.

We establish a unique stability criterion for the recycle set, and discuss the behavioral characteristics of the two 2-pass and two 3-pass autothermic reactors from standpoints of conversion and temperature distribution.

Problem Definition and Method of Mathematical Treatment

Four types of the most important autothermic reactors shown in Fig. 1 are dealt with, however, as will be seen later, the 3-pass double-pipe reactor can be coordinated into the 2-pass parallel-flow reactor with respect to optimum performance, and the two 2-pass reactors can be expressed as special cases in the 3-pass

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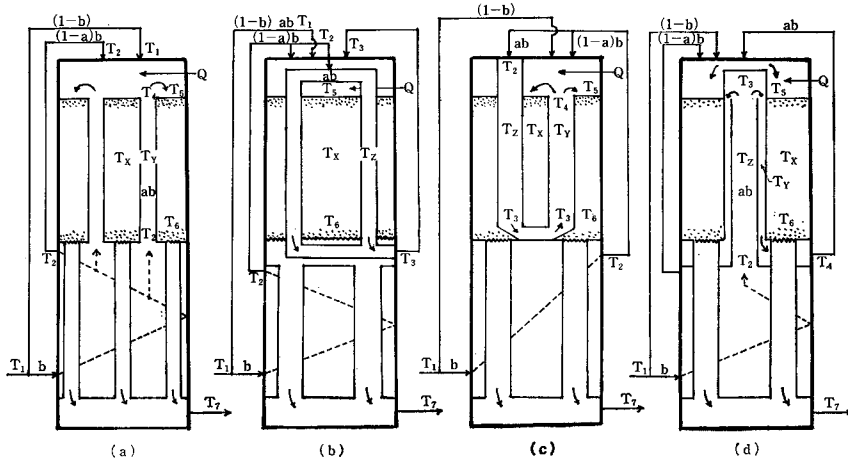(北海道大学水産学部化学工学講座)

Fig. 1. The schematic classification of the typical autothermic reactors.
  (a) The 2-pass counter-flow reactor.   (b) The 2-pass parallel-flow reactor.
  (c) The 3-pass mixed-flow reactor.   (d) The 3-pass double-pipe reactor.

mixed-flow reactor, the last 3-pass reeactor is treated first. For ease of problem solving, several assumptions are made without much loss of generality, as follows:

1. Steady state.
2. Plug flow with no axial heat transfer.
3. No radial heat resistance except at the tube wall and the adjacent films.
4. No heat gain from or loss to the surroundings.
5. Constant specific heat of reacting mass as a whole, irrespective of the composition and/or temperature.
6. Unimolecular exothermic reaction $A \rightleftarrows B$, whose reaction velecoty is $V = k_0 \exp\{-\varepsilon/(\theta+\theta_0)\} C_0 [1-X-X/\{K_0 \exp(\delta/(\theta+\theta_0))\}]$ occurring.
7. Overall heat transfer coefficients proportional to the 0.75th power of the mass velocities.

(No significant difference results from the assumption of bimolecular reaction as will be described in the following paper.)

Under these assumptions, a following nine simultaneous equations should hold for the 3-pass mixed-flow reactor:

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

$$\theta_6 = \theta_7 + b\theta_2 (= \Delta X + \theta_Q + b\theta_2) \tag{2}$$

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

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

$$\Delta X = X_f - X_i = \theta_7 - \theta_Q \tag{5}$$

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

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

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

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

where $V' = V/k_0 C_0$

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

$$\lambda = O; \ \theta_X = \theta_5, \ \theta_Y = \theta_4, \ \theta_Z = \theta_2$$
$$\lambda = \lambda_0; \ \theta_X = \theta_6, \ \theta_Y = \theta_Z = \theta_3$$

Notice that somewhat unusual dimensionless variables and parameters are used so that the effect of the catalyst bed length can be demonstrated.

Their solution proceeds as follows:
First assume θ_5. Assume θ_2 and find θ_4 in virtue of Eq. (4). Calculate θ_X, θ_Y, θ_Z along λ by the use of some suitable numerical method (Runge-Kutta-Gill method is used here). Apply any shooting method untill θ_Y equals θ_Z through varying θ_2 (the interval halving method is used here.). Use another θ_5 and repeat the whole procedure. Prepare sets of θ_2, θ_3, θ_4, θ_5, θ_6, θ_X, θ_Y, θ_Z and ΔX. Calculate θ_7 from Eqs. (1) and (2). The set of variables which gives the same value of θ_7 's within tolerable error is the solution required.

Operational Stability

As is well known not all the solutions of the above simultaneous equations are operationally stable. By assuming that the catalyst bed maintains invariably the temperature distribution specified by the steady state along the flow, van Heerden[3] presented a graphical method testing the stability shown diagrammatically in Fig. 2, where the curved line I shows the locus of the solutions of Eqs. (6), (7) and (8) on the θ_4–$(\theta_4 - \theta_2)$ plane and implies the heat generation by the reaction, whereas the straight line II denotes the relation among θ_2, θ_4 and $(\theta_4 - \theta_2)$, and expresses the heat removal by the reactant in the internal heat exchanger. Among their possible intersection(s) designating the solution of the above equations, the steady state consideration determines that points A and C are stable but point B is unstable because the angle between the tangent at the intersection to line I and the abscissa is less for A and C, and greater for B, than the one between line II and the axis.

Another criterion thus far not well known concerns with the relationship between the autothermic part and the external heat exchanger. Thus, in the same figure, the intersection(s) between the curvilinear line I' which denotes the relation between θ_2 and $(\theta_6 - \theta_2)$ from the solutions of Eqs. (6), (7) and (8), hence the heat generation by the reaction, and the straight line II' which designates the relation among θ_1, θ_2, and $(\theta_6 - \theta_2)$ and hence the heat removal by the reactant in the external heat exchanger, and the sign of the angle between the tangent to the line I' at the intersection(s) and the line II', dictate another solution(s) and the stability in such a way as A' and C' are stable but B' is unstable. However, as
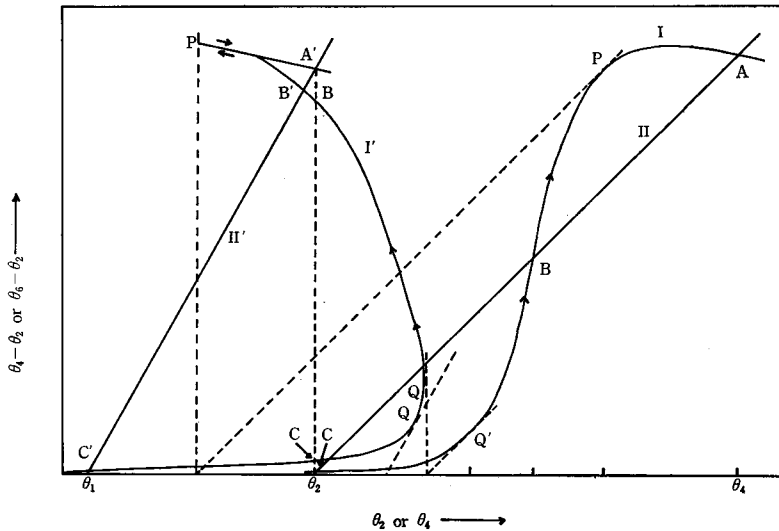
Fig. 2. Two criteria of the autothermic reactor and their relationship. The line I and I' expressed the solution of Eqs. (6), (7) and (8) on the θ_4-(($_4$-θ_2) plane and the θ_2-(θ_6-θ_2) plane, respectively. The line II has a slope of 45° and is drawn through θ_2 on the abscissa, and the line II' represents the solution of Eqs. (1) and (2) on the θ_2-(θ_6-θ_2) plane.

illustrated in the figure by borken lines, careful examination indicates that the first criterion corresponds to a vertical line in the second criterion which is understandable because no external heat exchanger is present. This clearly shows that the second criterion is more inclusive but nontheless more restrictive, and hence should be used in commerical reactors which exclusively have external heat exchangers.

Effect of Hest Transfer in Double Concentric Pipes in the Three-pass Double-pipe Reactor

Before proceeding further some comment must be made on the performance of the 3-pass double-pipe reactor.

The mathematical model is obtained by substituting Eqs. (6)', (7)' and (8)' written below for Eqs. (6), (7) and (8):

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

$$\frac{d\theta_Y}{d\lambda} = \beta_2(\theta_X - \theta_Y) - \beta_1'(\theta_Y - \theta_Z) \tag{7}'$$

$$\frac{d\theta_Z}{d\lambda} = -\beta_1'(\theta_Y - \theta_Z) \tag{8}'$$

subject to the boundary conditions:

$$\lambda = O; \ \theta_X = \theta_5, \ \theta_Y = \theta_Z = \theta_3$$

$$\lambda = \lambda_0; \quad \theta_X = \theta_6, \quad \theta_Y = \theta_4, \quad \theta_Z = \theta_2$$

As a matter of course, the stability criterion described above applies to this type of reactor. Kodama et al.[4,5,6,7] stated that a certain amount of β_1' is favorable based on their mathematical analysis which, for mathemetical ease, limited to cases where the chemical reaction rate does not depend upon temperature, or the activation energy is null. Unfortunately no unstable zone exists under their assumption, and the conclusion under practical conditions where the activation energy is considerable and the unstable zone does exist, has been left to scrutiny.
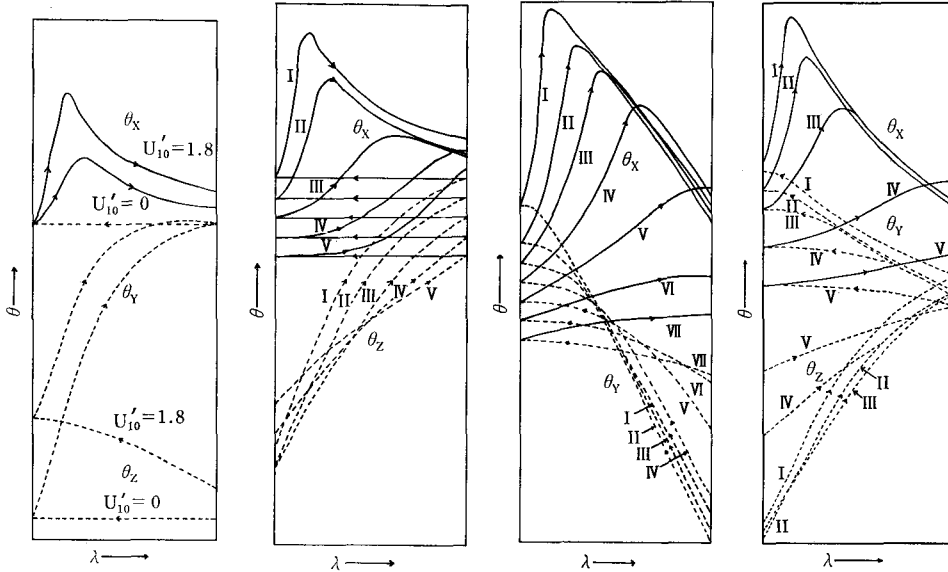

Fig. 3.   Fig. 4.   Fig. 5.   Fig. 6.

Fig. 3.   Effect of β_1' on the temperature profile of the 3-pass double-pipe reactor.
$$\beta_1' = U_{1,0}' F^{0.75} S_1'/(k_0 C_0 C_p), \quad U_{1,0}' = 0 \text{ and } 1.8$$
$$\beta_2 = U_{2,0} F^{0.75} S_2/(k^0 C^0 C_p), \quad U_{2,0} = 7.5$$
For the other parameters, see Table 1.

Fig. 4.   Temperature profile of the 2-pass parallel-flow reactor.   I at 770°K, II at 760°K, III at 750°K, IV at 740°K and V at 730°K expressed in θ_5.   Conversion shows max. at 750°K. $U_{2,0}=10.0$, $U_{1,0}=0$.   For other parameters, see Table 2.

Fig. 5.   Temperature profile of the 2-pass counter-flow reactor.   I at 750°K, II at 740°K, III at 730°K, IV at 720°K, V at 710°K, VI at 700°K and VII at 690°K expressed in θ_5.   Conversion has a max. at 740°K. $U_{1,0}=8.0$, $U_{2,0}=0$.   For other parameters, see Table 2.

Fig. 6.   Temperature profile of the 3-pass mixed-flow reactor.   I at 760°K, II at 750°K, III at 740°K, IV at 720°K and V at 700°K expressed in θ_5.   Conversion has a max. at 750°K. $U_{1,0}=U_{2,0}=6.0$.   For other parameters, see Table 2.

The results of the solution of Eqs. (6)', (7)' and (8)' with their boundary conditions disclose that the conversion is at its maximum when β_1' vanishes, at the boundary of the upper stable zone (Fig. 3 and Table 1), in which case the reactor

of this type reduces to a 2-pass parallel-flow reactor. This can be explained at least qualitatively by accepting that the counter-flow heat transfer between the inside and the outside of the inner tube tends to raise θ_3, which, in turn, raise θ_6 and the nearby downstream catalyst temperature, and eventually causes a lower conversion.

Table 1. *Maximum conversion (at point P) at various β_2 and β_1' values for the 3-pass double-pipe reactor.*

Condition: $C_0=4.44$, $X_i=0.054$, $F=920$, $C_p=10.6344$, $\Delta H=-7,000$, $k_0=0.5\cdot10^{-14}$, $E=40,000$, $K_0=0.4735\cdot10^{-2}$, $l=5$, $Q=0$, $a=b=0$, $S_2=17.2$, $S_1'=11.5$, ΔX in %

Notice that $U_2=U_{2,0}F^{0.75}$, $U_1'=U_{1,0}'F^{0.75}$, and $\beta_i=U_iS_i/(k_0C_0C_p)$

$U_{1,0}'$		$U_{2,0}$			
		7.5	9.0	10.5	13.5
0.0	$T_5=$	760	760	770	770
	$\Delta X=$	25.59	25.40	25.40	25.28
0.25	$T_5=$	760	760	770	770
	$\Delta X=$	25.46	25.51	25.26	25.25
0.50	$T_5=$	760	760	760	770
	$\Delta X=$	25.30	25.51	25.22	25.19
0.75	$T_5=$	750	760	760	770
	$\Delta X=$	25.25	25.45	25.36	25.10
1.0	$T_5=$	750	760	760	770
	$\Delta X=$	25.32	25.32	25.39	24.95
1.4	$T_5=$	750	760	760	760
	$\Delta X=$	25.30	25.11	25.30	25.20
1.8	$T_5=$	750	750	760	760
	$\Delta X=$	25.16	25.28	25.10	25.25
3.3	$T_5=$	740	740	750	750
	$\Delta X=$	25.00	25.00	25.12	25.28

Behavioral Characteristics of the Autothermic Reactors

When β_1 or β_2 vanishes in Eqs. (6), (7) and (8), they give the equations for 2-pass parallel-flow or counter-flow reactors, respectively.

The temperature profiles of the two 2-pass reactors and the 3-pass mixed-flow reactor are depicted in Figs. (4), (5) and (6).

There are some general features of particular interest regarding their shapes.

(1) At the boundary of the upper stable zone, P, maximum conversion is attained (Fig. 2), θ_2 is at its minimum (Figs. 2, 4, 5, 6), and the temperature profiles have negative gradient at the exit of the catalyst bed and shift monotonically upward with a decreased conversion, with the increase in θ_5 above that point (Figs. 2, 4, 5, 6).

(2) At the boundary of the lower stable zone, Q, θ_2 is at its local maximum (Fig. 2), and the temperature profile has approximately zero gradient at the bed exit (Figs. 4, 5, 6).

(3) From Q to P along the arrow, θ_2 tends to fall but with an increased conversion (Fig. 2), and the temperature profile has negative gradient at the bed exit (Figs. 4, 5, 6).

(4) At points below Q, θ_2 falls off with a decrease in conversion (Fig. 2), and

Table 2. *Maximum conversion (at point P) at various β_1 and β_2 values for the 3-pass mixed-flow reactor.*

Condition: $C_0=4.44$, $X_i=0.054$, $F=920$, $C_p=10.6344$, $\Delta H=-7,000$, $k_0=0.5\cdot10^{14}$, $E=40,000$, $K_0=0.4735\cdot10^{-2}$, $l=5$, $Q=0$, $a=b=0$, $S_1=8.6$, $S_2=8.6$, ΔX in %

Notice that $U_1=U_{1,0}F^{0.75}$, $U_2=U_{2,0}F^{0.75}$, and $\beta_i=U_iS_i/(k_0C_0C_p)$

$U_{2,0}$		$U_{1,0}$														
		0	1	2	3	4	5	6	7	8	8.5	9	10	11	11.5	12
0	$T_5=$	800	710	710	710	710	72 0	720	730	730	730	730	730	740	740	740
	$\Delta X=$	20.0	20.18	20.79	21.40	22.41	23.08	23.92	24.64	25.15	25.30	25.38	25.38	25.26	25.17	25.07
2	$T_5=$	370	710	710	720	730		730	740	740		750	750	770		780
	$\Delta X=$	20.85	21.45	22.15	22.99	23.73		25.10	25.54	25.78		25.83	25.77	25.65		25.53
4	$T_5=$	720	720	730	730	740		740	750	750		760	770	780		790
	$\Delta X=$	22.16	22.89	23.60	24.43	24.87		25.81	26.04	26.17		26.18	26.13	26.06		25.99
5	$T_5=$					740	740	750	750		760		770		770	
	$\Delta X=$					25.30	25.72	26.02	36.24		26.33		26.30		26.15	
6	$T_5=$	730	730	740	740	740	750	750	750	760	760	760	770	780		790
	$\Delta X=$	23.49	24.08	24.65	25.19	25.59	25.94	26.22	26.36	26.45	26.47	26.46	26.45	26.42		26.37
7	$T_5=$	730	740	740	740	750	750	750	760	760		760	780			780
	$\Delta X=$	23.96	24.54	25.06	25.42	25.82	26.16	26.33	26.46	26.56		26.57	26.56			26.52
8	$T_5=$	740		740		750	750	760	760		760		770	780	780	780
	$\Delta X=$	24.46		25.24		26.02	26.23	26.40	26.57		26.66		26.69	26.67	26.61	26.66
9.5	$T_5=$			750		750		760	760	760	770		770		780	
	$\Delta X=$			25.65		26.08		26.53	26.65	26.71	26.73		26.81		26.82	
10	$T_5=$	760	750													780
	$\Delta X=$	24.97	25.71													26.86
11	$T_5=$			750		760		760	760	770	770		770	780	780	780
	$\Delta X=$			25.72		26.23		26.56	26.63	26.74	26.79		26.88	26.89	26.91	26.91
12.5	$T_5=$	760		760		760		760	770	770	770		770		780	
	$\Delta X=$	25.32		25.85		26.27		26.46	26.61	26.74	26.79		26.89		26.94	
14	$T_5=$	760		760												780
	$\Delta X=$	25.47		25.93												26.71
15	$T_5=$	760		760		770		770	770	770			770		780	
	$\Delta X=$	25.59		25.90		26.04		26.41	26.54	26.64			26.77		26.87	
17.5	$T_5=$	760		770												780
	$\Delta X=$	25.49		25.67												26.69
18	$T_5=$	760														
	$\Delta X=$	25.40														
21	$T_5=$	770														
	$\Delta X=$	25.40														

the temperature gradient at the exit becomes positive (Figs. 4, 5, 6). Thus Q is thought to be the minimum permissible condition at which the autothermic part tends to raise its own temperature without resorting to an external heat exchanger, which necessarily functions to give negative temperature gradient at its exit, and with whose presence, Q shifts to still lower Q' (Fig. 2).

The above discussion is applicable to the 3-pass double-pipe reactor, although no data are presented.

Optimization

The 3-pass mixed-flow reactor which embraces the two 2-pass reactors as its extreme cases of $\beta_1=0$ and $\beta_2=0$, is investigated from a viewpoint of maximization of conversion. The results at various β_1 and β_2 values are summerized in Table 2. All the three reactors exhibit that their maximum conversions are attained at some appropriate values of β_1 and β_2, whereas the conversion of the 3-pass reactor is the highest of the three. The reaction trajectories at their maximum conversion on the θ-X plane (Fig. 7), disclose that the temperature spreads narrowest along the θ
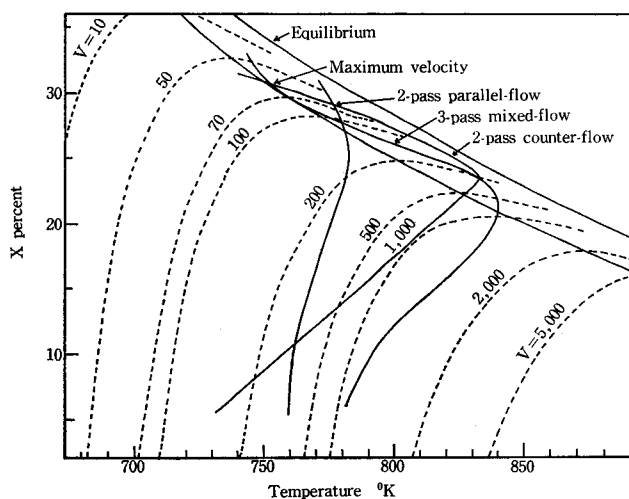

Fig. 7. Reaction trajectories on the O-X plane optimized with regard to β_1, β_2 and θ_5. $U_{2,0}=15.0$ for the 2-pass parallel-flow reactor, $U_{1,0}=10.0$ for the 2-pass counter-flow reactor, and $U_{1,0}=11.5$ and $U_{2,0}=12.5$ for the 3-pass mixed-flow reactor.

direction for the 2-pass parallel-flow reactor, wider for the 2-pass counter-flow reactor and the 3-pass mixed-flow reactor, while the temperature distribution of the 3-pass reactor is variable by changing β_1 and β_2 values with no significant loss of conversion.

The effect of various design and operation variables will be dicussed in a following paper.

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 the input reactant

C_0: Density of the input and the reacting mass at any location in kg-mol/m³

C_i: Concentration of the product in the input in kg-mol/m³

C_f: Concentration of the product in the output in kg-mol/m³

E: Energy of activation in kcal/kg-mol

F: Flow rate per unit catalyst cross-sectional area perpendicular to the flow direction in m³/m², h

ΔH: Heat of reaction assumed positive for an endothermic reaction in kcal/kg-mol

K_0: Apparent equilbirium constant at 0°K

k_0: Preexponential factor of the unimolecular rate constant in h⁻¹

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/m², h

R: Gas constant

S: Heat transfer area per unit cross-sectional area and per unit length of the catalyst bed in m²/m³

S_1: S between the catalyst bed and the cooling pipe in the counter-flow internal heat exchanger in m²/m³

S_2: S between the catalyst bed and the cooling pipe in the parallel-flow internal heat exchanger in m²/m³

S_1': S between the inner and the outer paths of the double-pipe heat exchanger in m²/m³

S_x: Heat transfer area of the external heat exchanger per unit cross-sectional area of the catalyst bed in m²/m²

T_i: Temperature at point i in °K (see Figs. 1, 2, 3, 4)

U_1: Overall heat transfer coefficient between the catalyst bed and the counter-flow cooling pipe in the internal heat exchanger in kcal/m², h, °K

U_2: Overall heat transfer coefficient between the catalyst bed and the parallel-flow cooling pipe in the internal heat exchanger in kcal/m², h, °K

U_1': Overall heat transfer coefficient between the inner and the outer paths of the double-pipe heat exchanger in kcal/m², h, °K

V: Unimolecular reaction rate in kg-mol/m³, h

V': Dimensionless unimolecular reaction rate

X_i: Initial mole fraction of the product, C_i/C_0

X_f: Final mole fraction of the product, C_f/C_0

ΔX: Conversion, $X_f - X_i$

β_i: Dimensionless heat transfer coefficient, $U_i S_i/(k_0 C_0 C_p)$

β_1': Dimensionless heat transfer coefficient, $U_i' S_i'/(k_0 C_0 C_p)$

γ: Dimensionless heat transfer coefficient, $U_X S_X/(F C_0 C_p)$

δ: Constant, C_p/R

ε: Constant, $C_p/E/R \, (-\varDelta H)$

λ: Dimensionless catalyst bed length, $k_0 l/F$

θ_i: Dimensionless temperature assuming $T_1=0$, $C_p(T_i-T_1)/(-\varDelta H)$

θ_0: Absolute dimensionless temperature corresponding to T_1, $C_p T_1/(-\varDelta H)$

θ_Q: Dimensionless temperature rise due to the added heat from outside, $C_p Q/(-\varDelta H)$

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