THE EFFECT OF INTERPARTICLE HEAT AND MASS TRANSFER ON THE BEHAVIOUR OF CATALYTIC ADIABATIC REACTORS WITH ENDOTHERMIC REACTIONS. I. THE REACTOR MODEL

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The effect of gas-particle heat and mass transfer on the reaction rate and the catalyst temperature in an adiabatic reactor with strongly endothermic reaction was studied using a mathematical model. It was found that subcooling of the catalyst surface against the reaction mixture is the prevailing phenomenon affecting the effectiveness factor and the longitudinal profile of the reaction rate.

The catalytic adiabatic chemical reactors are used in petrochemical industries to carry out strongly endothermic reactions. The steam reforming, (the reaction of methane with water steam), the reforming and platforming of gasoline and the dehydrogenation of butane or butene may serve as examples. In these processes the preheated reaction mixture enters the catalyst layer and reacts without any heat exchange between the catalyst layer and the surroundings. The process being strongly endothermic, heat is consumed in the catalyst particles and a significant temperature difference may occur between the catalyst particle and the gaseous reaction mixture.

The aim of this paper was an analysis of the effect of the gas-particle heat and mass transfer on the regime of a reactor with an endothermic reaction. The study is connected with the development of models for computer aided design of industrial reactors for the steam reforming.

THEORETICAL

A first order chemical reaction in a reaction mixture diluted with excess of inert gases was supposed to take place in an adiabatic plug flow reactor

$$A \rightarrow B \qquad \Delta H > 0 \,. \tag{1}$$

The reaction rate is a function of the partial pressure and the temperature at the external surface of the catalyst particle

$$R_s = k_s p_s \,. \tag{2}$$

The rate constant is a function of the surface temperature

$$k_s = k_i \exp\left[\frac{E\,(T_s - T_i)}{R\,T_s\,T_i}\right], \tag{3}$$

T_i is the inlet temperature in the bulk of the reaction mixture, k_i the value of the rate constant at this temperature, E the activation energy and R is the gas constant.

The bulk reaction temperature is a function of the degree of conversion

$$T = T_i + T_{ad} x \,. \tag{4}$$

The adiabatic temperature change of the reaction mixture T_{ad} is defined as

$$T_{ad} = \frac{(-\Delta H)\,N_i}{c_p}, \tag{5}$$

where ΔH is the reaction heat, N_i the inlet concentration and c_p the specific heat capacity.

The rate of the transfer of component A from the bulk to the catalyst surface is described by the equation

$$R_m = k_m A\,(p - p_s), \tag{6}$$

k_m is the mass transfer coefficient, A the exchange surface (i.e. the external specific surface of the catalyst) and p, p_s are partial pressures in the bulk and on the catalyst surface.

An analogous equation is used to describe the rate of the heat transfer from the catalyst surface to the reaction bulk

$$R_h = k_h A\,(T_s - T), \tag{7}$$

where k_h is the heat transfer coefficient and T, T_s the temperatures in the bulk respectively on the catalyst surface.

The following equalities must be satisfied in a steady state

$$R_m = R_s, \tag{8}$$

$$R_h = R_s\,(-\Delta H) \,. \tag{9}$$

Semidimensionless Model Equations

To analyse the reactor behaviour, the equations were rearranged in order to obtain either dimensionless parameters or parameters with dimension [K]. A dimensionless temperature was not introduced because the results became less illustrative when using a dimensionless temperature scale.

The following parameters were introduced:

$$P_1 = \frac{c_p R_i}{k_h A N_i}, \tag{10}$$

$$P_2 = \frac{k_h}{k_m (-\Delta H) p_i}. \tag{11}$$

The relative drop of the partial pressure between the reaction mixture and the catalyst surface than is

$$\frac{p - p_s}{p} = \frac{1}{1 - x} T_{ad} P_1 P_2 E_f \left(\frac{R_k}{R_i}\right), \tag{12}$$

where E_f is the effectiveness factor characterizing the effect of the gas-particle transfers. It is defined as the ratio of the reaction rate affected by the transfer processes to that unaffected, (i.e. the reaction rate in the kinetic region), compared at the local bulk temperature and partial pressure

$$E_f = \frac{R_s}{R_k}. \tag{13}$$

The ratio R_k/R_i will be called the adiabatic rate equation. It describes the effect of conversion, (i.e. the effect of the decrease of both the partial pressure and the bulk temperature), in the adiabatic regime on the reaction rate in the kinetic region.

The particle-surface temperature is affected by both the changes of the bulk temperature and the temperature drop between the gas and the catalyst particle, as follows

$$T_s = T_i + T_{ad} x + T_{ad} E_f P_1 \left(\frac{R_k}{R_i}\right). \tag{14}$$

If this equation is applied to the inlet state of the reaction mixture with the maximum possible effect of the heat and mass transfer the following limit conditions are fulfilled

$$x = 0 \quad \text{and} \quad p_s = 0 \tag{15}$$

and the following result is obtained

$$\frac{1}{P_2} = (T_s - T_i)_{max}. \tag{16}$$

The result says that the reciprocal value of the parameter P_2 indicates the maximum possible temperature difference which can occur between the bulk of the reaction mixture and the catalyst surface.

In the chemical engineering literature, the values of the heat and mass transfer coefficients are correlated in the form

$$\frac{k_m P M}{G_0} = 0.57 Re^{-0.41} Sc^{-0.66}, \tag{17}$$

$$\frac{k_h}{G_0 c_p} = 0.61 Re^{-0.41} Pr^{-0.66}, \tag{18}$$

where G_0 is the density of the mass flow, P the total pressure, M the mean molecular mass. The equations are valid in the region of a turbulent flow which is typical for petrochemical reactors.

Introducing these relationships the parameter P_2 can be expressed in the following form

$$\frac{1}{P_2} = \frac{0.57}{0.61}\left[\frac{c_p D_{AB} \rho}{\lambda}\right]^{0.66} \Delta T_{ad} = C \Delta T_{ad}. \tag{19}$$

Examples of the values of the constant C for petrochemical processes are shown in Table I.

Model of the Reactor

The plug flow model was used to simulate the behaviour of the reactor

$$\frac{dx}{d(W/W_s)} = P_3 E_f\left(\frac{R_k}{R_i}\right), \tag{20}$$

TABLE I
The values of the diffusion coefficients and constant C for the following mixtures[1,2]

Mixture	Mass ratio	D_{AB}, $cm^2 s^{-1}$	C
C_6H_{12}–H_2	1 : 1	2.6776	0.425
	1 : 2		0.392
	1 : 3		0.382
C_6H_6–H_2	1 : 1	3.156	0.456
	1 : 2		0.429
	1 : 3		0.420
CH_4–H_2O	1 : 2.5	2.231	1.078
	1 : 3		1.080
n-C_4H_{10}–H_2O	1 : 3	1.112	1.002

where W_s is the standard amount of the catalyst, W/W_s the relative longitudinal coordinate of the catalyst layer and P_3 the parameter defined as

$$P_3 = \frac{R_i W_s}{F p_i} R T. \qquad (21)$$

Its reciprocal value ($1/P_3$) can be interpreted as the dimensionless standard catalyst loading.

RESULTS AND DISCUSSION

Process Parameters

In developing a new process, the treated amount of the feedstock is usually prescribed. Then, there are only few technological parameters free to affect purposively the transport processes.

The model parameters and functions can be separated into two classes according to their possibilities to be changed:

1. Properties of the reaction mixture and the catalyst.

They can be changed either by varying the inlet composition or by using another catalyst. There are the following parameters in this group:

- adiabatic temperature change T_{ad},
- adiabatic rate equation R_k/R_i,
- dimensionless energy of activation E/RT_i,
- parameter P_2.

Parameter P_2 can be classified as independent of the reactor construction despite of the fact that heat and mass transfer coefficients are functions of the flow velocity, which in turn is determined by the reactor construction and load. The coefficients themselves are strongly dependent on the flow rate but their ratio changes only slightly.

2. Properties of the reactor and catalyst layer.

They can be affected by changing the reactor volume and diameter and by changing the shape and size of the catalyst particles. There are the following parameters in this class:

- amount of the catalyst W_s,
- volume flow rate of the reaction mixture F,
- parameter P_1.

Parameter P_1 is the coordinate locating the position of the regime between the kinetic and transfer ones. Its value is decisive for the effect of interparticle transport. The parameter involves the heat transfer coefficient which depends on the flow velocity and the specific external surface of catalyst. The limit value $P_1 \to 0$ indicates the kinetic regime. An increase of P_1 moves the regime towards the transfer controlled one.

The Effect of Parameter P_1 *on the reaction Rate*

There are two effects of the gas-particle transfer important from the technological point of view:

The reaction rate sinks with increasing value of parameter P_1 which is unfavourable for the reactor performance.

The catalyst surface temperature sinks which may be favourable because high surface temperature may accelerate the catalyst deactivation.

Examples of simulations are shown in Fig. 1. The reaction rate is plotted against the degree of the conversion for several values of the parameter P_1. In adiabatic reactors, the bulk reaction temperature sinks significantly with increasing degree of conversion, thereby decreasing the kinetic reaction rate R_k. Because the heat and mass transfer coefficients are insensitive to the temperature decrease, the effectiveness factor raises with increasing degree of conversion and the catalyst regime is moving towards the kinetic region. An example is given in Fig. 2. The effect of the heat and mass transfer on the catalyst-surface temperature is apparent in Fig. 3.

Examples of the effect of the parameter P_1 on longitudinal profiles of the degree of conversion, the catalyst surface temperature, the reaction rate and the effectiveness factor are shown in Figs 4 – 7.

Relationship between Heat and Mass Transfer Effects

Two types of effects are playing role simultaneously:

a) the particle surface is subcooled due to the endothermic reaction,

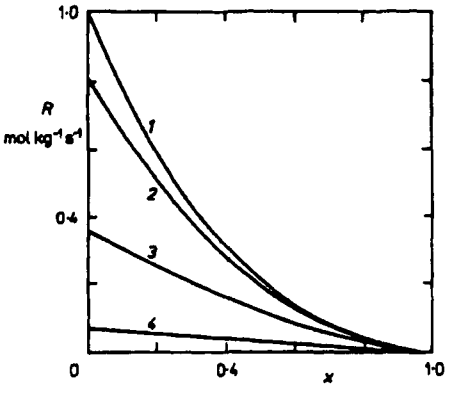

FIG. 1

Reaction rate as a function of the degree of conversation at different values of parameter P_1. *1* $P_1 = 0$ (kinetic reaction rate), *2* $P_1 = 0.1$, *3* $P_1 = 1$, *4* $P_1 = 10$

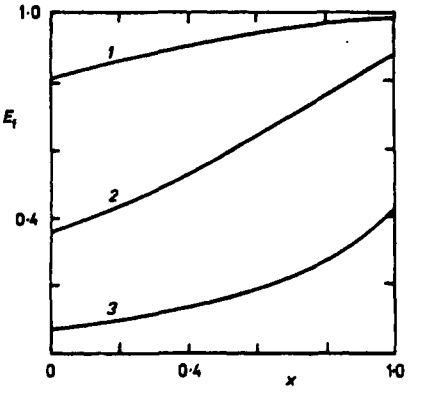

FIG. 2

Effectiveness factor as a function of the degree of conversion at different values of parameter P_1. *1* $P_1 = 0.1$, *2* $P_1 = 1$, *3* $P_1 = 10$

b) the partial pressures of the reactants at the particle surface are less than those in the bulk.

Both effects cause the reaction rate and the effectiveness factor to sink. For most strongly endothermic process (i.e. for reaction mixtures with large adiabatic temperature changes), the former effect prevails. To compare these effects, the relationship between the drop of the partial pressure between the gas and the catalyst surface and

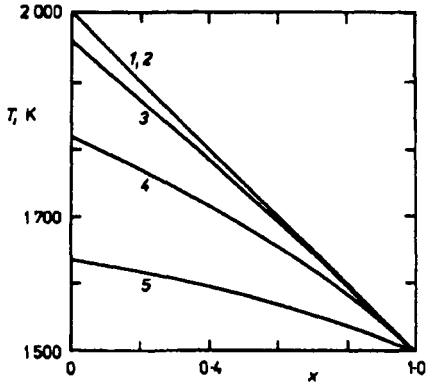

FIG. 3

The bulk temperature and the catalyst-surface temperatures as a functions of the degree of conversion at different values of P_1. *1* bulk temperature, *2*, *3*, *4*, *5* catalyst surface temerature, *2* $P_1 = 0$, *3* $P_1 = 0.1$, *4* $P_1 = 1$, *5* $P_1 = 10$

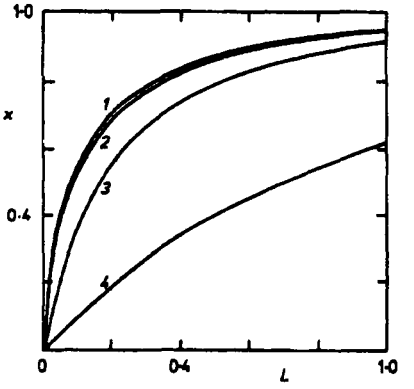

FIG. 4

The effect of the parameter P_1 on the longitudinal profiles of the degree of conversation. *1* $P_1 = 0$, *2* $P_1 = 0.1$, *3* $P_1 = 1$, *4* $P_1 = 10$

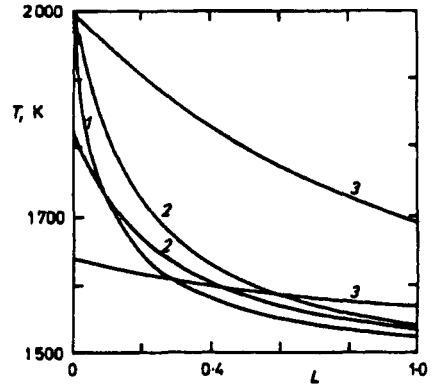

FIG. 5

The effect of the parameter P_1 on the longitudinal profiles of the bulk temperature (the upper curve) and the catalyst surface temperature (the lower curve). *1* $P_1 = 0$, *2* $P_1 = 1$, *3* $P_1 = 10$

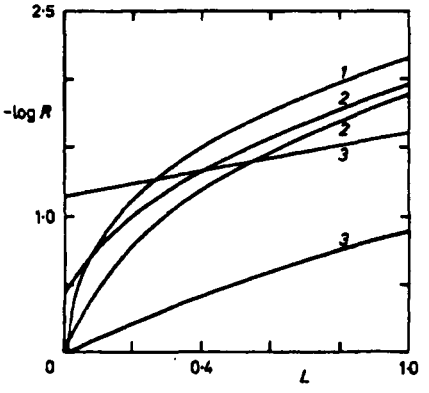

FIG. 6

The effect of the parameter P_1 on the longitudinal profiles of the reaction rate (the upper curve) and the reaction rate corresponding to the kinetic region (the lower curve). *1* $P_1 = 0$, *2* $P_1 = 1$, *3* $P_1 = 10$

the corresponding temperature drop, compared at the inlet end of the catalyst layer, can be estimated using the equation

$$\Delta T = \frac{\Delta p}{p_i} \frac{1}{P_2} . \tag{22}$$

The impact of these coupled changes on the reaction rate depends on the adiabatic temperature change, the energy of activation and the reaction order.

For the first order reaction the relative decrease of the reaction rate due to the increase of the partial pressure at the particle surface is

$$\Delta R_p = \frac{\Delta p}{p_i} , \tag{23}$$

the analogical decrease due to the decrease of the temperature is

$$\Delta R_T = 1 - \exp\left[\frac{\Delta T E}{R T_i (T_i + \Delta T)}\right] . \tag{24}$$

Combining these equations yields the ratio of the decreases

$$\Delta R_T / \Delta R_p = \left\{1 - \exp\left[\frac{E}{R T_i (T_i + \Delta T)} \frac{1}{P_2} \Delta R_p\right]\right\} / \Delta R_p . \tag{25}$$

The result indicates that for the first order reaction a unique parameter determines the ratio of the sensitivities. Its simplified form is

$$\frac{E}{R T_i^2} \frac{1}{P_2} = \frac{E}{R T_i^2} C \Delta T_{ad} . \tag{26}$$

Examples of the ratio are shown in Fig. 8.

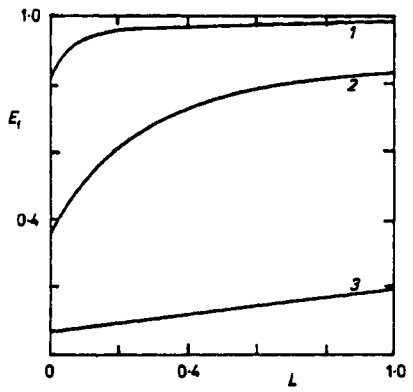

FIG. 7

The effect of the parameter P_1 on the longitudinal profile of the effectiveness factor. *1* P_1 = 0.1, *2* P_1 = 1, *3* P_1 = 10

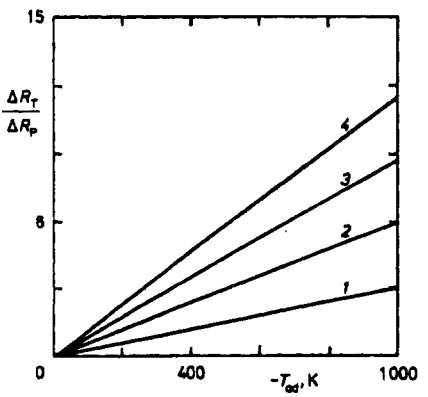

FIG. 8

The effect of the adiabatic temperature change on the ratio $\Delta R_T/\Delta R_p$ (Eq. (25)) for different values of activation energy. *1* E = 50 000, *2* E = 100 000, *3* E = 150 000, *4* E = 200 000

Effects of the Gas-Particle Heat Transfer in Reactors Heated through the Reactor Wall

Many strongly endothermic reactions are carried out in tubular reactors heated in the radiation chamber of a furnace or heated by a suitable heat carrier. In these reactors no significant temperature differences can be formed between the gas and the catalyst, the effect of a partial pressure drop is also negligible.

The cause consists in the fact that all reaction heat which is transferred from the reaction mixture to the catalyst surface must be transferred from the tube external surface to the reaction mixture. The driving force of the heat transfer between the tube external surface and the reaction mixture being constrained to protect the tube from damage, the process becomes heat transfer limited.

There are two causes that the driving force of the gas-particle heat transfer is much smaller than that between the reaction mixture and the tube external surface:

1. The heat transfer area for the tube-wall transfer is much smaller than that of the gas-particle heat transfer. Supposing that spherical particles are applied the relationship of the heat transfer areas is

$$\frac{A_{\text{cat}}}{A_{\text{wall}}} = 1 - \frac{3}{2}\frac{D_{\text{tube}}}{D_{\text{cat}}} . \tag{27}$$

2. The heat transfer resistance between the tube external surface and the reaction mixture is augmented by the resistance of the wall. Petrochemical reactors are operated at high flow velocities and the wall resistance represents a substantial part of the overall resistance. Supposing that the following condition is valid

$$\frac{k_{\text{h,cat}}}{k_{\text{h,wall}}} \approx 2 , \tag{28}$$

TABLE II

The values of the parameters used in simulations (if another values were used they are given in the text of the figures)

Parameter	Symbol	Dimension	Value
Energy of activation	E	J mol^{-1}	100 000
Adiabatic temperature change	T_{ad}	K	-500
Inlet temperature	T_{i}	K	2 000
Parameter 1	P_1	-	0; 0.1; 1; 10
Parameter 2	P_2	K^{-1}	-0.002
Amount of the catalyst	W	kg	28
Flow rate	F	m^3 s^{-1}	0.03

the ratio of the driving forces of the heat transfer is

$$\frac{\Delta T_{cat}}{\Delta T_{wall}} = \frac{A_{tube}}{A_{cat}} \frac{k_{h,tube}}{k_{h,cat}} < 0.1 \qquad (29)$$

Even in the case that the wall temperature drop were 200 K, the temperature difference between the reaction mixture and the catalyst surface would be less than 20 K.

The situation is different in adiabatic reactors. Preheated mixture enters the catalyst layer and the reaction heat is removed from the reaction mixture without the necessity to be transferred through the tube wall.

SYMBOLS

A	external specific catalyst surface, $m^2\ kg^{-1}$
C	constant
c_p	specific heat capacity, $J\ kg^{-1}\ K^{-1}$
D	diameter, m
D_{AB}	diffusion coefficient, $m^2\ s^{-1}$
E	activation energy, $J\ mol^{-1}$
E_f	effectiveness factor
F	feed rate of the reaction mixture, $m^3\ s^{-1}$
G_0	mass flow density, $kg\ s^{-1}\ m^{-2}$
H	reaction heat, $J\ mol^{-1}$
k	rate constant in the bulk of reaction mixture, $mol\ kg^{-1}\ s^{-1}\ Pa^{-1}$
k_i	inlet rate constant in the bulk of reaction mixture, $mol\ kg^{-1}\ s^{-1}\ Pa^{-1}$
k_h	heat transfer coefficient, $J\ s^{-1}\ m^{-2}\ K^{-1}$
k_m	mass transfer coefficient, $mol\ Pa^{-1}\ s^{-1}\ m^{-2}$
k_s	rate constant on the catalyst surface, $mol\ kg^{-1}\ s^{-1}\ Pa^{-1}$
L	dimensionless length of the catalyst layer
M	mean molecular mass, $kg\ kmol^{-1}$
N_i	inlet concentration, $mol\ kg^{-1}$
P	total pressure, Pa
Pr	Prandtl number
P_1	parameter
P_2	parameter, K^{-1}
P_3	parameter
p	partial pressure in the bulk of reaction mixture, Pa
p_i	inlet partial pressure, Pa
p_s	partial pressure on the catalyst surface, Pa
R	gas constant, $J\ mol^{-1}\ K^{-1}$
Re	Reynolds number
R_h	rate of heat transfer, $J\ kg^{-1}\ s^{-1}$
R_i	inlet reaction rate in kinetic region, $mol\ kg^{-1}\ s^{-1}$
R_k	kinetic reaction rate, $mol\ kg^{-1}\ s^{-1}$
R_m	rate of the mass transfer, $mol\ kg^{-1}\ s^{-1}$

ΔR_p	relative decrease of the reaction rate due to the partial pressure drop
R_s	reaction rate on the catalyst surface, mol kg^{-1} s^{-1}
ΔR_t	relative decrease of the reaction rate due to the temperature drop
Sc	Schmidt number
T	temperature in the bulk of reaction mixture, K
T_{ad}	adiabatic temperature change, K
T_i	inlet temperature, K
T_s	temperature on the catalyst surface, K
x	degree of conversion
W	amount of catalyst, kg
W_s	total amount of catalyst, kg
λ	heat conductivity, W m^{-1} K^{-1}
ρ	density, kg m^{-3}

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