

## CHARACTERISTICS FOR EVALUATING THE REACTOR REGIME WITH ENDOTHERMIC REVERSIBLE REACTION

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Criteria are proposed in the paper for evaluating the reactor regime (with endothermic reversible reaction, heated by radiation of combustion products) from thermodynamic and kinetic points of view. The limiting reactor regimes in which the controlling process is the process kinetics or the heat transfer are defined. The effect of the catalyst activity on the reactor output and the surface temperature of the reaction tube and the effect of heat input power of the reactor radiation section on the conversion and the surface temperature of the tube are discussed. The results are verified on a simplified mathematical model of steam reforming and employed to discuss the selection of the regime of an industrial reactor.

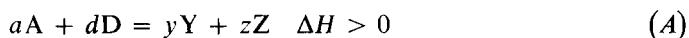
When designing reactors with a reversible endothermic reaction or comparing the results achieved in different reactors with the results of mathematical modelling, it is necessary to find a firm basis for this comparison. The comparison only on the basis of, *e.g.*, outlet conversion is imperfect. Therefore it is necessary to compare simultaneously the fundamental parameters of the regime for which the given information holds.

The aim of this work is to carry out the analysis which enables to define the fundamental parameters by means of which it is possible to classify the reaction conditions.

### THEORETICAL

#### *Mathematical Model of Reactor*

A simplified model of tube reactor heated by combustion products was used for the analysis. It is assumed that a sole endothermic heterogeneously catalyzed chemical reaction of the type



takes place in the reactor for which the dependence of the equilibrium constant on temperature,

$$K = f(T), \quad (I)$$

is known. To describe the kinetics of the reaction, the equation in the form

$$R = r/r_0 = (1 - x) \exp\left(\frac{E(T - T_0)}{RTT_0}\right) \left(1 - \frac{p_Y^y p_Z^z}{p_A^a p_D^d K}\right) \quad (2)$$

was used. Substance A was chosen as a key component.

It is assumed that the combustion products and the reaction mixture flow co-currently by the piston flow, and the mechanism of transfer by radiation is decisive for the heat transfer between the combustion products and the outer tube surface. Heat is transferred by conduction and convection from the outer surface of the tube into the reaction mixture. Heat losses to surroundings are neglected. The process takes place in steady state.

The balance equations of the key component, heat of reaction mixture, and heat of combustion products were rearranged for calculations to a form in which the scale of temperatures is retained but the other quantities and parameters were rearranged so as to be either dimensionless or to have in their dimension only K.

Let us define the dimensionless length of the reaction tube:

$$L = (k_s A_h l T_0^4) / (F c_p L_c), \quad (3)$$

the relative activity of catalyst:

$$A = (W r_0 c_p) / (n_{A0} k_s A_h T_0^4), \quad (4)$$

the adiabatic temperature drop:

$$T_{ad} = (-\Delta H) n_{A0} / c_p \quad (\text{K}), \quad (5)$$

the parameters of regime:

$$B = F_s c_{ps} / (F c_p), \quad (6)$$

$$C = k_h / (k_s T_0^4) \quad (\text{K}^{-1}). \quad (7)$$

For the balance of the key component then holds

$$dx/dL = AR, \quad (8)$$

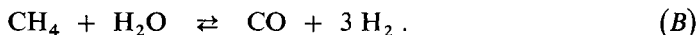
for the thermal balance of the reaction mixture

$$dT/dL = AT_{ad}R + C(T_t - T), \quad (9)$$

and for the thermal balance of the combustion products

$$dT_s/dL = -\frac{C}{B}(T_i - T). \quad (10)$$

A mathematical simulation was carried out for the following concrete case:



Parameters:  $K = 1.598 \cdot 10^{11} \exp(-27\,101/T)$ , standard state chosen as pure component at the system temperature and pressure of 1 MPa;  $T_0 = 1\,000\text{ K}$ ,  $T_{\text{ad}} = 1\,000\text{ K}$ ,  $E = 90\,000\text{ J}$ ,  $P = 3.7\text{ MPa}$ ,  $T_i = 800\text{ K}$ ,  $T_{\text{si}} = 2\,400\text{ K}$ .

## RESULTS AND DISCUSSION

### *Thermodynamic Characteristics of Regime*

Under the above assumptions, the reaction mixture forms an adiabatic system with the combustion products. The heat taken away from the combustion products passes to the reaction mixture, where it is employed either to heating the mixture or to converting the substances. From the thermodynamic point of view, the ratio of the heat brought into the process to that necessary for the course of the chemical reaction is decisive.

To describe the thermodynamic conditions of the process, it is possible to use more characteristics. One of them is the highest possible initial temperature of the reaction mixture,  $T_p$ ,

$$T_p = (T_i + BT_{\text{si}})/(B + 1). \quad (11)$$

This temperature would be reached if the temperature of the reaction mixture equalized with the temperature of the combustion products without chemical reaction.

Further thermodynamic characteristic is the lowest final temperature of the reaction mixture,  $T_k$ ,

$$T_k = (T_i + BT_{\text{si}} - T_{\text{ad}})/(B + 1). \quad (12)$$

This temperature would be reached if the temperature of the reaction mixture equalized with the temperature of the combustion products in case of conversion  $x = 1$ .

For a reversible reaction, the final equilibrium conversion  $x_r$  and the final equilibrium temperature  $T_r$  corresponding to it form the key characteristics of the reactor regime. Those are the values which would be reached by the system if the chemical equilibrium were established at equalized temperature of the reaction mixture and the combustion products.

At the given inlet composition of the reaction mixture (and known value of equilibrium constant), it is sufficient to give two data of the temperature regime, e.g.

the final equilibrium conversion and the highest initial temperature  $T_p$  or the value of  $T_p$  and  $B$  to characterize the regime from the thermodynamic point of view. The relationships between these two quantities are illustrated in Fig. 1.

To achieve high equilibrium conversion at given values of inlet temperature of reaction mixture  $T_1$  and inlet temperature of combustion products  $T_{si}$ , it is necessary to increase the ratio of the flow rate of combustion products to the flow rate of reaction mixture (the value of  $B$ ) – see Fig. 2. With increasing  $B$  the highest initial temperature  $T_p$  and the total heat capacity of the system increases, too, and the adiabatic temperature drop of the system for which holds

$$T_{ads} = T_{ad}/(B + 1) \quad (13)$$

decreases.

#### *Classification of Regime from Thermodynamic Point of View*

With regard to the final equilibrium conversion, it is advantageous to divide the regimes into two groups:

The regime with practically irreversible behaviour of chemical reaction

$$x_r \rightarrow 1, \quad T_r \rightarrow T_k. \quad (14)$$

In case of this regime, excess heat is supplied into the radiation part of the furnace.

The regime with reversible behaviour of chemical reaction:

$$x_r < 1, \quad T_r > T_k. \quad (15)$$

In case of this regime, the highest attainable outlet conversion is limited by the heat supply into the radiation part of the reactor.

#### *Practical Aspects of the Choice of Thermodynamic Characteristics of Regime*

The use of the regime with reversible behaviour of reaction limits the outlet conversion because

$$x_e < x_r \quad (16)$$

must hold, however, at the same time provides the following advantages: The outlet temperature of reaction mixture, products of combustion, and tube surface are limited thermodynamically and cannot reach high values (Figs 3, 4). Consequently, the danger of overheating the reaction tube at the outlet end does not occur. Simultaneously the temperature of the combustion products decreases along the whole tube length, and therefore the thermal efficiency of the furnace increases. The regime is

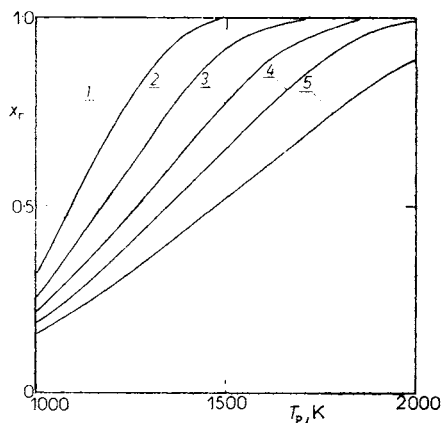


FIG. 1

Relation between the highest initial temperature of reaction mixture, parameter  $B$  and equilibrium conversion;  $B$ : 1 5, 2 2, 3 1, 4 0.5, 5 0.1

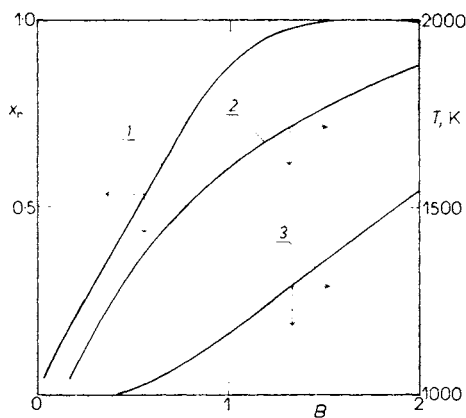


FIG. 2

Effect of excess of combustion products ( $B$ ) on 1 the equilibrium conversion, 2 the highest possible initial temperature of mixture  $T_p$ , and 3 the equilibrium temperature of mixture  $T_r$  for  $T_{si} = 2200$  K

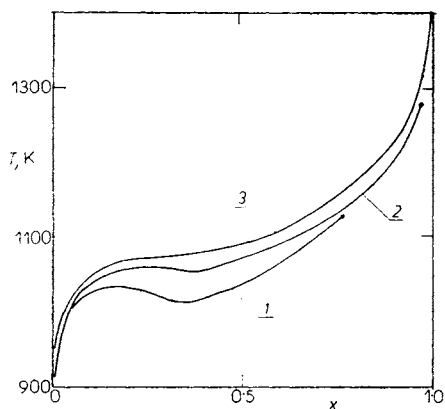


FIG. 3

Effect of excess of combustion products ( $B$ ) on the temperature of reaction mixture and conversion. Illustration of passing from the region of reversible behaviour 1 to the region of irreversible behaviour 3;  $A = 0.01$ ,  $C = 0.1$ ,  $B$ : 1 0.9, 2 1.4, 3 2.0

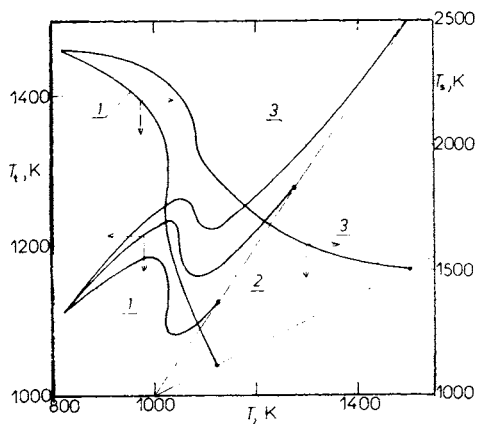


FIG. 4

Effect of excess of combustion products ( $B$ ) on the temperature of reaction mixture  $T$ , temperature of tube wall  $T_t$ , and temperature of combustion products  $T_s$  (phase plane);  $A = 0.01$ ,  $C = 0.1$ ,  $B$ : 1 0.9, 2 1.4, 3 2.0

milder because the surface temperature of tubes is lower, and the danger of overheating at their beginning is diminished. The highest possible initial temperature of the reaction mixture reaches lower values, too (Figs 3, 4).

It is possible to use an excess of catalyst because even a prolongation of reaction time cannot bring about the overheating of reaction mixture and reaction tube at its end (Figs 5, 6) for both the outlet conversion and the outlet temperature are limited thermodynamically. Therefore the catalyst deactivation manifests itself at the reactor outlet only very little. Only if the catalyst activity decreases so much that it appears at the outlet, it is necessary to compensate the activity decrease by increasing the flow rate of combustion products, *i.e.*, by shifting the regime towards the region with irreversible behaviour (Fig. 7).

If the thermodynamic regime is chosen in the region of irreversible behaviour, it is possible to increase the conversion arbitrarily, which is advantageous. However, the regime exhibits even considerably disadvantageous features of behaviour: In the region of high conversions, the reaction mixture loses the ability to cool the tube surface, the temperature of reaction mixture increases, and the reaction tube is overheated (Figs 3, 4). Therefore it is necessary to limit the outlet conversion by increasing the reactor load so much that the outlet conversion could not approach unity for kinetic reasons.

The outlet temperature of combustion products is high because for thermodynamic reasons

$$T_{sc} > T_k \quad (17)$$

must hold. The thermal efficiency of the radiation chamber is consequently low (Fig. 4). The highest possible initial temperature of the mixture is high, therefore the dangerous region of the tube overheating (Fig. 4) may arise in the front part of the reaction tube where the mixture has already been heated but the combustion products are still hot.

If the catalyst is deactivated in a process, the use of regime with irreversible behaviour requires an active way of controlling when the reactor load is changed according to the instantaneous catalyst activity so that the outlet conversion may not fall below the required value. However, simultaneously it is necessary to ensure the overheating of the reaction tube neither on its near end nor on its outlet end to take place owing to the decrease of the catalyst activity (Figs 5, 6).

#### *Classification of Regime from Kinetic Point of View*

From the kinetic point of view it is possible to regard the process as a system of successive processes: 1. heat transfer *a*) by radiation from combustion products to the outer surface of tube, *b*) by conduction through the tube wall, *c*) by convection from the inner tube wall to the reaction mixture. 2. Reversible chemical reaction.

In the system of successive processes, it is possible to define the limiting regimes in which the slower of steps is the step determining the rate of process, the second one being practically in equilibrium. The following limiting regimes exist:

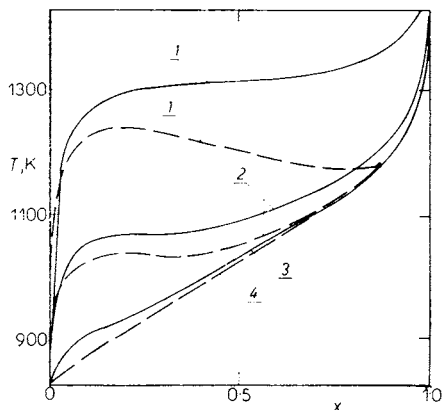


FIG. 5

Effect of relative catalyst activity ( $A$ ) on the dependence of reaction temperature on conversion in region of irreversible behaviour ( $B = 2$ ; —) and reversible behaviour ( $B = 1.1$ ; - - -). Illustration of passing from the kinetic region 1 to the transfer region 4 owing to the increasing catalyst activity;  $C = 0.05$ ,  $A$ : 1 0.001, 2 0.01, 3 0.06, 4 0.08

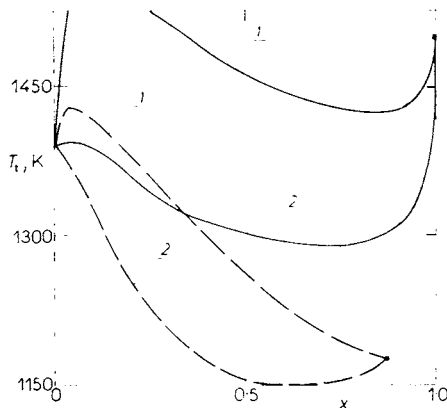
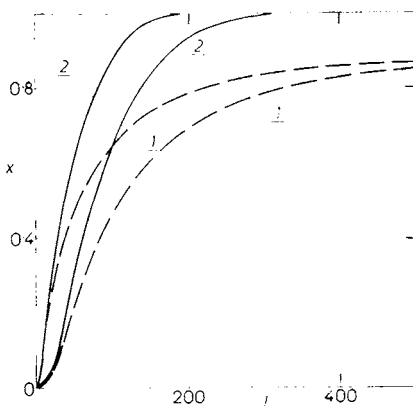


FIG. 6

Effect of the relative catalyst activity on the dependence of surface temperature of tubes on the conversion;  $C = 0.05$ ,  $B = 2$  (—, region of irreversible behaviour),  $B = 1.1$  (- - -, region of reversible behaviour);  $A$ : 1 0.001, 2 0.06

FIG. 7  
Effect of the relative catalyst activity on the dependence of conversion on the length of reactor;  $B = 2$  (—, irreversible behaviour),  $B = 1.1$  (- - -, reversible behaviour),  $C = 0.05$ ,  $A$ : 1 0.001, 2 0.06



*Kinetic regime.* Such a regime is concerned when the chemical reaction is very slow compared to heat transfer, the heat transfer is then practically in equilibrium, which means that the temperatures of combustion products, reaction tube, and reaction mixture are equalized, and the relation

$$T = T_t = T_s \quad (18)$$

holds. The rate of process is determined by the reaction rate corresponding to the temperature following from the balance relation

$$T = BT_{s_i} + T_i - T_{ad}x/(B + 1). \quad (19)$$

*Regime controlled by heat transfer.* If the chemical reaction is very rapid compared to the heat transfer, the controlling process is the heat transfer from products of combustion into the reaction mixture, and the chemical reaction is practically in equilibrium. The local temperature of the reaction mixture is the equilibrium temperature corresponding to the local conversion:

$$T = T_r(x), \quad (20)$$

and the rate of process is determined by the rate of heat transfer at this temperature.

#### *Possibilities of Influencing the Regime by Choosing Parameters*

The kinetic characteristics of regime which determine the distance from the limiting regimes are in the mathematical model concentrated in parameters  $A$  and  $C$ . Parameter  $A$  expresses the ability of chemical reaction to consume heat to the ability of combustion products to radiate to the tube surface. Parameter  $C$  then determines the division of resistances to heat transfer.

The radiation of combustion products is determined by the properties of substances, to a certain degree by the design of combustion chamber (which can be changed only minimally), and by the temperature of combustion products. At the same time it is, however, desirable to reach high thermal efficiency of furnace, *i.e.*, the outlet temperature of combustion products to be as low as possible. For these reasons it is not possible to influence significantly the rate of transfer by radiation.

Nor is it possible to change significantly the heat passage through the wall of reaction tube because the wall thickness and its thermal conductivity are predetermined by the requirements of mechanical strength and thermal endurance.

The heat transfer coefficient inside the tube depends on the flow rate of reaction mixture, *i.e.*, on the reactor load. This quantity, however, is limited by the reactor



output required. The flow rate could be influenced significantly only by changing the reactor design (tube length), which is, however, made impossible by the given dimensions of radiation chamber.

Therefore from the analysis follows that the position between the kinetic and transfer regime can be significantly changed just by the catalyst activity, *i.e.*, by its composition, increasing its bulk density or decreasing its grain diameter (in case of internal diffusion). On using a highly active catalyst, the reactor regime is shifted towards the transfer region in which the limiting step is the rate of heat transfer by radiation and further increasing the catalyst activity exerts then only small influence on the reactor output (Figs 5–7).

However, another situation is in ensuring the thermal protection of the reaction tube where the high catalyst activity can be decisive because it reduces the heat stress of the reaction tube in inlet part. In the outlet part of the reaction tube, the effect of the catalyst activity is more complex because it depends on the thermodynamic regime. In the region of reversible behaviour, the end temperature of tube wall is of little sensitivity to the catalyst activity because it is limited thermodynamically. In the region of irreversible behaviour of reaction, for  $x_e < 0.9$ , the increase in catalyst activity results in decreasing the tube-wall temperature (the heat consumption in chemical reaction is increased). For the outlet conversion  $x_e > 0.9$ , the reaction mixture is already nearly reacted through, it cools little the reaction tube, and the surface temperature increases extremely along with the increasing outlet conversion. Therefore a danger is imminent of overheating the tube at its end (Figs 5, 6).

## CONCLUSION

It follows from the above analysis that the endeavour to develop an especially active catalyst is not reasonable because high catalyst activity is not exploited in reactor. To ensure the required reactor output, it is not necessary to know the accurate information on the catalyst activity or on the reaction kinetics as far as the catalyst activity is sufficiently high for the regime to approach the transfer region. Further increase in activity is already inappropriate. However, very important is the catalyst durability, *i.e.*, its deactivation resistance.

Simultaneously it is proved that for practical use, it is more advantageous to use the regime with reversible behaviour of chemical reaction and to employ the regimes with irreversible behaviour only in case of high catalyst deactivation to prolong its life-time. Their application, however, requires a more thorough way of control because it is necessary to observe the course of the tube surface temperature, and accordingly, to adjust the reactor load and the heat input power so as the overheating of the reaction tubes not to occur.

## LIST OF SYMBOLS

- A* parameter defined by relation (4)  
*A<sub>h</sub>* reaction tube surface through which heat is transferred, m<sup>2</sup>  
*B* parameter defined by Eq. (6)  
*C* parameter defined by Eq. (7), K<sup>-1</sup>  
*c<sub>p</sub>* specific heat, J kg<sup>-1</sup> K<sup>-1</sup>  
*E* activation energy, J mol<sup>-1</sup>  
*F* mass flow, kg s<sup>-1</sup>  
 $\Delta H$  heat of reaction, J mol<sup>-1</sup>  
*K* equilibrium constant  
*k<sub>h</sub>* heat transfer coefficient from outer surface of reaction tube into reaction mixture, W m<sup>-2</sup> K<sup>-1</sup>  
*k<sub>s</sub>* heat transfer coefficient by radiation from combustion products to outer surface of reaction tube, W m<sup>-2</sup> K<sup>-4</sup>  
*L* dimensionless length of reaction tube from its beginning to a given place  
*L<sub>c</sub>* total length of reaction tube, m  
*l* distance from the beginning to a given place of tube, m  
*n<sub>A0</sub>* initial concentration of key component, mol kg<sup>-1</sup>  
*P* total pressure, MPa  
*P<sub>i</sub>* partial pressure of component *I*, MPa  
*R* dimensionless reaction rate  
*R* gas constant, J mol<sup>-1</sup> K<sup>-1</sup>  
*r* reaction rate, mol kg<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>  
*r<sub>0</sub>* reaction rate at a basic temperature *T<sub>0</sub>* and *x* = 0; catalyst activity, mol kg<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>  
*T* temperature, K  
*T<sub>ad</sub>* adiabatic temperature drop of reaction mixture, K  
*T<sub>k</sub>* lowest possible end temperature of reaction mixture, K  
*T<sub>0</sub>* basic temperature, K  
*T<sub>p</sub>* highest possible initial temperature of reaction mixture, K  
*W* catalyst mass, kg  
*x* conversion of key component

## Subscripts

- e* outlet value  
*i* inlet value  
*r* equilibrium value  
*s* combustion products  
*t* outer surface of reaction tube  
 quantities without subscript — reaction mixture

Translated by J. Linek.