Simulation of the coke burning process on the catalyst grain

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Abstract. Based on the kinetic model of oxidative regeneration of coked catalysts, a two-phase diffusion mathematical model of the oxidative regeneration process of coked catalysts in a catalyst grain has been constructed. A numerical analysis of the grain heating in a wide range of the initial oxygen concentration, the inlet temperature, VHSV of the gas has been carried out. It has been established that the process of coke burning has a high parametric sensitivity to the initial oxygen concentration.

1. Introduction

By reason of economic sanctions by foreign manufacturers, studies on the reactivation of coked catalysts become relevant. The most common technological method is the burning of coke deposits with oxygen-containing air. The process of coke deposits burning is non-stationary, and often, due to large thermal casts, dangerous, abnormal situations arise. It is necessary to determine the possible maximum heating for various initial coke deposits. The conducting of special experiments on plant units is unprofitable, and sometimes dangerous. Therefore, to assess the possible heating levels, computer simulation methods are used.

2. Kinetic model of coke burning

The kinetic model of the coke burning process is a set of elementary stages, reactions and equations that characterize the dependence of the rate of chemical transformation on the reaction parameters: pressure, temperature, concentrations of reagents, etc. These dependencies are determined on the basis of experimental data in the field of the reaction parameters change.

The kinetic model is the first level of the model of any reactor and the basis for mathematical models at the catalyst grain level and a fixed bed.

In the practice of mathematical modeling of oxidative regeneration, kinetic models are used, obtained on the basis of an empirical approach [1, 2, 3]. Such models represent a quantitative dependence of the main reaction rate (burning of coke) and rather accurately approximate the experimental data only in the studied range of conditions.
The coke burning rate during the regeneration of coked catalysts \( \left( \frac{dq_c}{dt} = -w \right) \), determined mainly as a kinetic equation: 

\[
w(T, C, q_c) = k_0 \cdot \exp\left(-\frac{1500...22000}{T}\right) \cdot C \cdot q_c^n
\]  

(1)

where \( T \) - temperature, \( K; C \) and \( q_c \) - oxygen and coke concentrations, respectively; \( k_0 \) - preexponential which dimension depends on the dimension \( C \) and \( q_c \).

Carbon order \( (n) \) varies widely: \( n = 1 \) in works \([7, 8, 9]\), \( 1 < n < 2 \) in a work \([11]\) and \( n < 1 \) - in works \([11, 16]\). The mechanism for changing the reaction order is associated with the “aging” of coke during the regeneration process as residual hydrogen burns out, a significant effect of which on the coke burning out rate was noted \([2]\) in an experimental study of the oxidative regeneration patterns.

A more rigorous approach in the development of an empirical kinetic model was used in \([10]\). The authors believe that coke contains two components: slow-burning - pure carbon and light-burning - hydrocarbon fragments of the structure \( CH_\gamma \). The empirical kinetic model presented in this work is the only one described in the literature that reflects the experimentally discovered fact: an increase in the content of carbon monoxide in oxidized products with increasing temperature. However, with low-temperature coke burning (480°C and below), this model gives clearly elevated concentrations of \( CO \).

Empirical models are useful for engineering practice and can be used to solve some modeling problems \([11-15]\). Based on them, many regularities of oxidative regeneration of catalysts have been studied, reaction orders for the main reagents have been evaluated, and data on activation energies have been obtained. At the same time, the kinetics of formation and interconversion of the products of burning are little studied. The main drawback in studying the kinetics of oxidation of coke deposits on catalysts is the narrow range of variation of the determining parameters: the initial degree of coking, oxygen concentration, and especially temperature.

A sufficiently reliable kinetic model of coke burning, which allows to calculate not only the rate of coke removal, but also the composition of the gas phase in the regenerator with the necessary accuracy, was presented in \([19]\). In this work, an analysis of the patterns of the aluminosilicate cracking catalysts oxidative regeneration was carried out. The surface of these catalysts does not have a noticeable effect on the individual products formation rate of coke oxidation. On the basis of the experimentally discovered patterns of coke burning from the surface of catalysts, a detailed representation of the oxidative regeneration process in the form of cumulative separate stages is given.

3. Scheme of chemical transformations and the corresponding kinetic rate equations for the stages

The scheme of chemical transformations describing the oxidation of coke deposits of some averaged formula, and the corresponding kinetic rate equations for the stages have the form \([19, 20]\):

\[
\begin{align*}
2\theta_c + O_2 & \rightarrow 2\theta_{CO} & \quad W_1 = k_1(T) \cdot \theta_1^2 \cdot x_i \\
\theta_{CO} + O_2 & \rightarrow \theta_{CO} + CO_2 & \quad W_2 = k_2(T) \cdot \theta_2 \cdot x_1 \\
\theta_{CO} & \rightarrow \theta_c + CO & \quad W_3 = k_3(T) \cdot \theta_3 \\
\theta_{CH_\gamma} + O_2 & \rightarrow \theta_{CO} + H_2O & \quad W_4 = k_4(T) \cdot \theta_4 \cdot x_1 \\
\theta_{CO} + \theta_{CO} & \rightarrow 2\theta_c + CO_2 & \quad W_5 = k_5(T) \cdot \theta_5^2 \\
\theta_{CH_\gamma} \leftrightarrow \theta_c + z_{H_2} & \quad W_6 = k_6(T) \cdot \frac{P_c}{R_c} \cdot (\theta_6^1 - z_i) \\
\theta_{CO} \leftrightarrow \theta_c + z_0 & \quad W_7 = k_7(T) \cdot \frac{P_c}{R_c} \cdot (\theta_7^1 - z_2)
\end{align*}
\]  

(2)
where $W_i - \text{rate of separate stages, } \frac{\text{mol}}{m^2 \cdot \text{sec}}$ for $W_i - W_j$ and $\frac{g}{m^2 \cdot \text{sec}}$ for $W_i - W_j; k(T) - \text{temperature-dependent rate constants } (T)$ according to the Arrhenius equation (the dimension $k_i(T)$ coincides with the dimension $W_i$); $X_j - \text{oxygen concentration in the gas phase, mole fraction; } Z_i - \text{hydrogen concentration } (z_1 = z_{H_2}) \text{ and oxygen } (z_2 = z_O) \text{ in the bulk of coke deposits, } \frac{z_j}{z}; \theta_i - \text{degrees of coke surface coverage with various carbon complexes } (\theta_i = \theta_{CH_2}) - \text{hydrogen-carbon complex, } \theta_i = \theta_{CO} - \text{oxygen-carbon complex, } \theta_i = \theta_C - \text{free carbon surface); } \theta'_i - \text{amount of coke adsorbed by hydrogen } (k = 1) \text{ and oxygen } (k = 2), \text{ equilibrium relative to the current state of the surface of the coke deposits, } \frac{g}{g}; \rho_C - \text{coke density, } \frac{g}{m^3}; R_c - \text{average radius of coke grains, m.}$

The developed kinetic models of the process of oxidative regeneration (2) are quite reliable theoretically reasonable [11, 21] models.

4. Models of coke burning on catalyst grain

In the practice of mathematical modeling of the process of oxidative regeneration, the identification of coke burning patterns on the catalyst grain is given serious attention. The main question of interest to researchers is what overheating is possible with the regeneration of catalyst grains depending on the choice of initial conditions: the mass of deposited coke, grain size, gas temperature and oxygen content in it. Another important issue is the influence assessment of the of heat and substance transfer processes in the grain pores on the nature and the coke burning rate.

Most often in early studies (15 ... 20 years ago) in modeling the regeneration process on catalyst grains [5, 8, 9] various modifications of a layer-by-layer burning model were used: a narrow or localized combustion zone moving along the grain radius of the oxidation reaction front and etc. In justifying the choice of such a model, one usually proceeds from the following premises [9, 17]. At high temperatures, the coke burning rate begins inhibited by the rate of oxygen transport to the oxidation surface. In the case of a spherical grain, the reaction proceeds along a spherical interface that moves to the center of the grain. The total reaction rate is limited by the rate of oxygen diffusion through the pores of the grain freed from coke to the chemical reaction zone. Oxygen is consumed and no further diffusion to the center of the grain occurs. Experimental data that qualitatively illustrate the described above character of coke removal are given in [22]. However, the regeneration of coked catalysts is not always carried out in the intradiffusion mode. If you start the coke burning process with low initial oxygen concentrations [9, 18] to prevent possible overheating, the coke removal rate is about the same at any point along the grain radius. The model of layer-by-layer combustion cannot reproduce a similar pattern of coke burning. Such models are a rather rough simplification of the physical picture of the coke burning in the catalyst bed, and the results obtained with their help can be considered only as qualitatively correct estimates.

More rigorous for modeling the regeneration process at the catalyst grain level should be considered an approximation within the framework of one or another variant of the diffusion model [10, 16]. The material balance equations of this model take into account the free oxygen diffusion in the grain pores; at the same time chemical reactions occur in which oxygen is consumed. For physical reasons, the diffusion model seems to be more rigorous in comparison with the layer-by-layer burning model. For oxygen diffusion, there are no barriers in the form of a narrowly localized reaction zone. Therefore, there is no need to involve additional assumptions to derive the motion equation of the reaction zone. Despite the simpler formulation of the problem, the diffusion model includes the layer-by-layer burning model as a limiting case. Indeed, it is always possible to choose such conditions of the process that the coke burning will take place practically in layers, as was shown in [10].

The constants given in the Table 1 contain unknown parameters - the initial radius and the specific surface of the coke granules. Since during regeneration the catalyst is initially with different coking
level, these values are not constant. To eliminate ambiguity, the constants are recalculated using dependencies (3).

Table 1. The kinetic model constants (2) for an aluminosilicate catalytic cracking catalyst.

| $k_1$ | $k_1$ (520°C), sec$^{-1}$ | $E_1$, kJ/mol |
|-------|-------------------------|---------------|
| k1    | 0.112                   | 99.1          |
| k2    | 0.563                   | 90.8          |
| k3    | 0.220                   | 52.8          |
| k4    | 0.315                   | 50.4          |
| k5    | 1.890                   | 27.3          |
| k6    | 5.923                   | 154.5         |
| k7    | 1.890                   | 42.7          |

\[
S_k = S_k^o \cdot \left( \frac{q_c^*}{q_c^o} \right)^2; \quad R_c = R_c^o \cdot \left( \frac{q_c^o}{q_c^*} \right)^3
\]  
(3)

Let's choose as some standard values ($R_c^o$ and $S_k^o$) - the initial radius and specific surface of coke deposits for the catalyst with initial coking $q_c^o = 3\%$ (wt.), for which the constants given in Table 1 are determined. Then, when calculating the coke burning with $q_c^o$, different from $q_c^*$, it is sufficient to multiply the kinetic constants describing the diffusion into the bulk of coke by the factor $\frac{S_k^o}{S_k} = \left( \frac{q_c^o}{q_c^*} \right)^2$, and the rest $\mathcal{R}$, by the factor $\left( \frac{q_c^o}{q_c^*} \right)^3$.

5. Evaluation of the maximum heating on the grain and in the fixed catalyst bed

All researchers involved in the process modeling at the catalyst grain level, raise the question of the maximum heating on the catalyst grain [1, 2, 8]. The interest in this problem is clear: overheating of the catalyst causes its cracking, which reduces the mechanical strength and activity and leads to an increase in the catalyst consumption. The predictive power and simulation results, obtained under the assumption that regeneration does not change the pore structure and the grain size of the catalyst, lose their predictive power.

To estimate the heating of the catalyst grain using the mathematical description (4) - (5) with the boundary conditions (6) - (7), calculations were performed, the results of which are presented in the form of dependences in Figure 1, Figure 2, Figure 3 and Figure 4.

\[
\begin{align*}
\frac{dy_i}{dt} & = -\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D \frac{\partial y_i}{\partial r} - r^2 \mu y_i \right) + \frac{\gamma_i S_k}{C_n} \sum_{j=1}^{n} V_j W_j \\
C_k \frac{\partial T_i}{\partial t} & = \frac{\lambda_k}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T_i}{\partial r} \right) + \gamma_k S_k \sum_{j=1}^{n} Q_j W_j \\
t & = 0: y_i = 0, T_i = T_v; r = 0: D \frac{\partial y_i}{\partial r} = 0, \lambda_k \frac{\partial T_i}{\partial r} = 0; \\
r & = R_i: D \frac{\partial y_i}{\partial r} - \mu_k y_i = \beta(x_i - y_i) - \mu_k Y_i \\
Y_i = \{ x_i \text{ at } \mu_k < 0 \text{ or } y_i \text{ at } \mu_k > 0 \} \\
\lambda_k \frac{\partial T_i}{\partial r} & = \frac{\lambda_k}{S_{10}} \frac{\partial T_i}{\partial T} + \alpha(T_i - T_v) \\
I & = 0: \lambda_{ex} \frac{\partial T_i}{\partial T} = \alpha_{ex}(T_i - T_v); \ I = L_r : \lambda_{ex} \frac{\partial T_i}{\partial T} = 0
\end{align*}
\]
The following parameter set is chosen as the basic one: $q_0 = 5\%$ (mas.), $x_i^0 = 2.0\%$ (vol.), $T = 500\, ^\circ C$, $d = 5$ mm. In the calculations, one of the parameters was variable and the other three were constant values. The obtained dependences of the maximum heating of the grain on the values of the main parameters are in good agreement with the data of literary sources [1, 2, 9].

The dependence of the maximum heating $\Delta T$ on the inlet temperature $T_0$ is interesting - a characteristic S-shaped curve that reaches the asymptotic line when the temperature rises. A similar curve was obtained for dependence $\Delta T$ on oxygen concentration $x_i$, however, the parametric sensitivity ($\Delta T$ on $q_0$) is higher than for ($\Delta T$ on $T$). Although this result is characteristic of strongly-
thermal-gas-phase combustion processes [23, 24], the combustion of a condensed medium (coke) once
again confirms the thermodynamic generality of the combustion problems.

![Figure 4. The change in the heating of the catalyst grain during regeneration depending on grain diameter.](image)

It is usually assumed [9, 10] that the heating of the catalyst rises with an increase in the amount of
coke deposits to a certain limit. The dependence $\Delta T \propto q_c^0$ we obtained from (Figure 3) accurately
reflects the described character of the dependence ($\Delta T \propto q_c^0$), and the asymptotic, almost horizontal
section is reached at $= 10\%$ (wt.).

The dependence of heating on the grain size $d_1$ is qualitatively identical to the dependence ($\Delta T$
on $q_c^0$) which coincides with the data of [18]. The above results refer to the case of a uniform coke
distribution along the catalyst grain radius. In fact, this is not entirely correct. Data on the
experimental study of the coke distribution along the radius of bead cracking catalysts are given in
[18]. It was shown that under all conditions the periphery of the bead grain is getting more coked than
its central zone.

6. Conclusion
A technique for mathematical modeling of the oxidative regeneration process of coked catalysts within
fixed bed equipment has been developed. A two-phase diffusion mathematical model of the coke
burning process was built, which takes into account the change in the reaction volume and the
resulting mass transfer by an additional (Stephan) flow. The numerical analysis of the maximum
heating on the grain and within the catalyst bed was carried out with change in the wide range of the
initial oxygen concentration, the inlet temperature, VHSV of the gas flow, the catalyst coking level
and the diameter of its grain. It is shown that the process of oxidative regeneration has a high
parametric sensitivity to the initial oxygen concentration.

7. References
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