THE RATE OF FORMATION OF A SURFACE DEPOSIT IN AN ELONGATED CHEMICAL REACTOR

(UDC 541.124)

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Translated from Doklady Akademii Nauk SSSR, Vol. 166, No. 1,
pp. 151-154, January, 1966
Original article submitted August 16, 1965

Hollow reactors of high length to diameter ratio are frequently employed in carrying out large scale chemical reactions, especially in the petroleum industry. Here the principal chemical reaction responsible for the generation of the desired product takes place within the body of the reactor. The type of turbulence generally met in practice is such that there is little alteration in the concentrations of the materials participating in this reaction as one moves out along a diameter, and the reactor can therefore be described in terms of a one-dimensional ideal displacement model. There are, however, certain cases of practical interest in which effects of the walls and transverse transfer are quite significant. The present paper deals with one such situation, namely, that in which catalytic action or local superheating gives rise to intensive side reactions, with the eventual deposition of a film or deposit on the wall surface. Reactions of this kind account for only a small fraction of the overall transformation in an efficient chemical operation and they can, therefore, be neglected in evaluating the yield of the desired product at any one point; they do lead, however, to a reduction in the reactor diameter and thus require production breaks which it is desirable to reduce as far as possible.

Thermal cracking and pyrolysis are examples of reactions of the type in question here. It is characteristic that these processes are carried out at Mach numbers less than unity, the largest value, 0.3, being obtained in the ethane to ethylene pyrolysis. These reactions are carried out in wall-heated tubular reactors where they lead to a gradual formation of coke deposits on the wall surfaces. Other examples are found in processes for the production of acetylene which are now in development, where it is observed that coke and carbon black are deposited on the wall surfaces at a continually increasing rate. Here it is no longer a matter of heating through the reactor walls and the flow of gas proceeds through the reactor at sonic speeds. Deposit formation is due, in both cases, to sequential (usually bimolecular) chemical reactions which lead to products of higher and higher molecular weight, with the eventual formation of a new solid phase which fails to pass back into the reactor space.

This list of examples could be extended to include processes in which the reaction of products present in the gaseous phase results in the deposition of a thermally stable covering. The prevention of wall deposition is also a problem of importance for the operation of organic liquid heat interchangers and in applications of organic coding agents, especially in high energy nuclear reactors.

An important factor in the choice of optimal conditions for such reactions is the relation between the rate of growth of the surface deposit, the composition of the products present in the reactor, and the hydrodynamic conditions prevailing in the course of the reaction. It is especially important to be able to interpret the various, experimentally observed types of flow velocity relations. This problem is studied in the present paper on the basis of a model reaction, the method proposed in [1] being used to assure retention of the basic characteristics of actual chemical reactions of the type under study here.

We will now consider new phase (film) formation on the surface of a tubular reactor, limiting consideration to the case in which mechanical transfer can be neglected and formation is slow in comparison with the rate of production of the desired product in the interior of the reactor. One can draw on the model kinetic system of Table 1

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TABLE 1. Model Reaction for New Phase Formation on a Surface

Reaction	Reaction rate law	
	in bulk	on surface
Reaction of substance a with the formation of product b	$k_I(T)a$	–
Formation of a high-molecular substance c	$k_{II}(T)b^2$	$\varkappa_{II}(T_s)b_s^2$
Formation of a surface deposit (substance d)	–	$\varkappa_{III}(T_s)c_s$

to characterize the set of reactions occurring in either gaseous and liquid phases and, at the same time, retain the principal features of the effects in question here. Bulk concentrations are designated in this table by the same letter as is used for indicating the particular substance in the chemical equation, and the subscript s indicates that the quantity in question is evaluated at r = R, R being the reactor radius. The coefficients of molecular diffusion of substances a, b, c, and d are assumed to be related through the equations:

$$D^a \cong D^b \gg D^c, \quad D^d = 0. \tag{1}$$

The relatively low value of D^C traces back to the high molecular weight of Substance d, the solid phase precursor.*

When the Peclet number averaged over the reactor cross section is high, we follow [1] and divide the flow into a basic core and various diffusional and thermal boundary layers, these with the respective layer depths δ_i (i = a, b, c) and δ_T. The subscript v is used to designate those core parameters which depend only on the distance, x, from the reactor entrance. In view of the inequalities of (1), it can be considered that

$$\delta_c < \delta_a, \quad \delta_b, \quad \delta_T. \tag{2}$$

In addition, δ_a and δ_b are less than δ_T when the value of the Prandtl number is high. At radii so large that curvature can be neglected, one can draw on [1] and the above remarks concerning the chemical reactions to write the transfer equations as:

$$\begin{aligned} u(x, r)\frac{\partial a}{\partial x} &= \frac{\partial j_r^a}{\partial r} - k_I(T)\,a \qquad \text{in layer} \quad \delta_a, \\ u_*(x, r)\frac{\partial b}{\partial x} &= \frac{\partial j_r^B}{\partial r} + k_I(T)\,a - k_{II}(T)\,b^2 \ \text{in layer} \quad \delta_b, \\ u_*(x, r)\frac{\partial c}{\partial x} &= \frac{\partial j_r^c}{\partial r} + k_{II}(T)\,b^2 \qquad \text{in layer} \quad \delta_c. \end{aligned} \tag{3}$$

The term j_r^C designates the radial flow of substance c. The boundary conditions at the tube surface have the form

$$\begin{aligned} D^a \partial a/\partial r\,|_{r=R} &= 0, \\ D^b\,\partial b/\partial r + \varkappa_{II}(T_s)\,b^2\,|_{r=R} &= 0, \\ D^c\,\partial c/\partial r - \varkappa_{II}(T_s)\,b^2 + \varkappa_{III}(T_s)\,c\,|_{r=R} &= 0. \end{aligned} \tag{4}$$

A second set of boundary conditions is obtained from the requirement that the concentrations at the inner boundary layer surface be the same as in the reaction space. To this approximation, the left-hand members of the equations of (3) can be set equal to zero, the distance required for appreciable alteration of concentration being comparable with the reactor length, l, and much greater than the reactor diameter. The considerations advanced in [1] indicate that it is also permissible to neglect contributions from bulk chemical reactions in the first two of the equations of (3). These approximations are expressed by the inequalities

$$\sqrt{k_I / D\delta} \ll 1, \quad \sqrt{k_{II} b / D\delta} \ll 1, \tag{5}$$

in which we have, for compactness, set

$$D^a = D^b = D, \quad \delta_a = \delta_b = \delta.$$

It can be assumed that these inequalities are almost always satisfied in practice.†

* Asphaltens with molecular weights as high as 2000 are found in the coke which is formed in cracking; these are converted into insoluble carboides on the reactor walls.

† In cracking, for example, k < 10 sec^{-1}, D $\sim 5\cdot10^{-5}$ for a liquid, and $\sim 10^{-3}$ for a gaseous, phase with $\delta \leqslant 10^{-3}$ cm.

With these approximations and boundary conditions for (3), one finds the following expressions for the boundary layer concentrations of substances a and b:

$$a(x, r) = a_v(x), \quad b(x, r) = \frac{b_v(x) - b_s(x)}{\delta}(R - r) + b_s(x) \quad \text{when } R - r < \delta, \tag{6}$$

where

$$b_s(x) = \frac{D}{2\varkappa_{II}(T_s)\delta}\left[\sqrt{1 + \frac{4\varkappa_{II}(T_s)\delta}{D} b_v} - 1\right]. \tag{7}$$

Condition (2) justifies the approximation of T by T_s and b by b_s in the last of the equations of (3), thus leading to

$$c(x, r) = -\frac{1}{2}\frac{k_{II}(T_s)b_s^2}{D^c}(\delta_c - R + r)^2 + c_1(\delta_c - R + r). \tag{8}$$

The problem at hand is such that c_v can be set equal to zero, and the x dependence of C_1 determined from the condition

$$-k_{II}b_s^2\delta_c + D^c c_1 - \varkappa_{II}(T_s)\, b_s^2 + \varkappa_{III}(T_s)\left[-\frac{k_{II}(T_s)b_s^2\delta_c^2}{2D^c} + c_1\delta_c\right] = 0;$$

from this it follows that

$$c_1 = \frac{\varkappa_{II}(T_s)b_s^2 + k_{II}(T_s)b_s^2\delta_c + \varkappa_{III}(T_s)k_{II}(T_s)b_s^2\delta_c^2/2D^c}{\delta_c\varkappa_{III}(T_s) + D^c}. \tag{9}$$

An expression for the rate of deposit formation, w, per unit surface area is obtained from these equations:

$$w = \varkappa_{III}(T_s)c_s = \frac{\varkappa_{III}b_s^2}{\varkappa_{III} + D^c/\delta_c}(\varkappa_{II} + k_{II}(T_s)\delta_c), \tag{10}$$

b_s being determined from (7). The second factor of (10) is such as to permit two possibilities for formation of the intermediate c, either directly through catalytic reaction, at the wall, or within the c boundary layer. The form of the denominator of the first factor reflects a competition between the various c to d reactions and transfer of c back into the reactor space. Two limiting cases arise in practice:

$$b_v \ll D/\varkappa_{II}(T_s)\delta, \quad b_s \cong b_v; \tag{11'}$$

$$b_v \gg D/\varkappa_{II}(T_s)\delta, \quad b_s \cong \sqrt{(D/\varkappa_{II}(T_s)\delta)\, b_v}. \tag{11''}$$

Substitution of (11) into (10) leads to various limiting forms for the relation between rate of deposit formation and depth of boundary layer, these ranging from direct proportionality to δ_c (kinetic regime) to inverse proportionality to δ (diffusional regime). Alteration in the flow rate can lead to either an increase or a decrease in the rate of deposit formation in an elongated reactor with variable wall temperature, conditions in the reactor varying from one place to another.

The equations deduced above are also applicable to flow around a body of arbitrary form, provided the approximations adopted for the elongated reactor are still valid. Thus flow around a nonstreamlined spherical or cylindrical object can lead to deposit formation at the leading edge in some regimes and at the rear edge in others.

Introduction of the expressions for δ and δ_c given in [2] is all that is required for obtaining more precise relations in the hydrodynamic characteristics for each particular case.

LITERATURE CITED

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