A. G. Gorelik

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The radial temperature profiles and their stability conditions were investigated for a layer of granular packing through which heat was being generated in a length of pipe.

An important problem in investigating tubular chemical reactors with packings of granular catalysts is the determination of the permissible pipe radius for thermal stability. Difficulties can arise because the heat generation increases exponentially with temperature, whereas the rate of heat removal varies linearly with temperature. The general equation for the heat balance can be written as

$$
\begin{equation*}
\lambda_{\text {eff. } .} \frac{\partial^{2} t}{\partial z^{2}}+\lambda_{\text {eff.r }}\left(\frac{\partial^{2} t}{\partial r^{2}}+\frac{1}{r} \cdot \frac{\partial t}{\partial r}\right)-w_{\mathrm{g}} \mathrm{c} \mathrm{~g} \frac{\partial t}{\partial z}+\sum_{i=1}^{n} h_{i} \psi_{i}=0 \tag{1}
\end{equation*}
$$

The analysis [1] treats separately the diffusion (depending on thermal conductivity) axially and radially through the layer. This separate treatment does not distort the results and it allows Eq. (1) to be simplified for analyzing radial heat transfer as follows

$$
\begin{equation*}
\lambda_{\mathrm{eff.r}}\left(\frac{\partial^{2} t}{\partial r^{2}}+\frac{1}{r} \cdot \frac{\partial t}{\partial r}\right)-\operatorname{ceg}_{\mathrm{g}} c_{\mathrm{g}} \frac{\partial t}{\partial z}+\sum_{i=1}^{n} h_{i} \psi_{i}=0 \tag{2}
\end{equation*}
$$

For most cases the permissible pipe radius can be determined from the temperature distribution through that section at the center of which the maximum axial temperature ("hot spot") occurs [2].

By analogy with [3] it maybe assumed that the temperature exhibits a maximum at all radii in the section in which this "hot spot" occurs. In this case $\partial t / \partial z=0$. It should be noted that the condition $\partial t / \partial z=0$ is satisfied in any section of the pipe reactor in which there exists axially isothermal flow, for example, because of catalytic reduction $[4,5]$. The case in which the heat generation over the section is constant and does not depend on temperature was considered in [6]. In this case the temperature distribution over the section is found to be parabolic and the wall temperature of the pipe is given by

$$
\begin{equation*}
t_{\mathrm{w}}-t_{\mathrm{m}}=\frac{Q r_{0}}{2 \alpha} \tag{3}
\end{equation*}
$$

The pipe wall temperature does not then depend on the thermal conductivity of the packing; it increases linearly with the pipe radius.

During chemical reaction the heat generation varies with temperature in accordance with the Arhenius law. For zeroth-crder reactions an analytical solution for cases of low heat loss can be obtained using the method of "separation of exponents" [7]. The problem for third-order boundary conditions at the pipe surface is analogous to that with divergent heating [8]. A similar problem but with a first-order boundary equation and heat-transfer dependent only on the mean temperature over the section has also been analyzed [9]. This analysis is however imprecise and it is more accurate to use the present equation for the calculation of true temperature profiles over the section for third-order boundary conditions and parametric

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Fig. 1. Dependence of $\theta_{\text {cr. }}, \theta_{\mathrm{cr} .}, \theta_{\mathrm{cr} . \mathrm{a}} / \theta_{\mathrm{cr} . \mathrm{w}}$, $\delta_{\mathrm{cr}}, \sigma_{\mathrm{cr}}$ on Bi , for variable heat generation.
values which determine the heat generation and transfer. The problem is treated as follows [8]:

$$
\begin{gather*}
\frac{d^{2} \theta}{d \rho^{2}}+\frac{1}{\rho} \cdot \frac{d \theta}{d \rho}=-\delta e^{\theta},  \tag{4}\\
\frac{d \theta(0)}{d \rho}=0  \tag{5}\\
-\frac{d \theta(1)}{d \rho}=\operatorname{Bi} \theta(1) \tag{6}
\end{gather*}
$$

Here

$$
\theta=\frac{E\left(T-T_{\mathrm{m}}\right)}{R T_{\mathrm{m}}^{2}} ; \quad \delta=\frac{h E k r_{0}^{2}}{\lambda_{\mathrm{eff.}} R T_{\mathrm{m}}^{2}} ; \quad k=k_{0} \exp \left(-E / R T_{\mathrm{m}}\right) .
$$

The solution of (4)-(6) takes the form:

$$
\begin{equation*}
\theta=\ln \frac{8}{\delta\left[\exp (-\mu) \rho^{2}+\exp \mu\right]^{2}} \tag{7}
\end{equation*}
$$

where $\exp (-\mu)=\sqrt{ } \sigma ; \sigma$ is the root of the characteristic equation

$$
\begin{equation*}
\frac{8 \sigma}{\delta(\sigma+1)^{2}}=\exp \frac{4 \sigma}{\operatorname{Bi}(\sigma+1)} . \tag{8}
\end{equation*}
$$

This equation has two roots but only the smaller relates to a steady solution. Having found a value of $\delta$ from (8) and also having derived $\sigma$, it is possible to determine the value of $\sigma_{\text {cr }}$ corresponding to the critical value of the parameter $\delta_{\mathrm{cr}}$. The corresponding equation for $\sigma_{\mathrm{cr}}$ is

$$
\begin{equation*}
\sigma_{\mathrm{cr}}=\frac{-2+\sqrt{4+\mathrm{Bi}^{2}}}{\mathrm{Bi}} \tag{9}
\end{equation*}
$$

For values of $\delta>\delta_{c r}$ stable conditions cannot be obtained (the process diverges). These values limit the stability in any given situation. The values of $\sigma_{\mathrm{cr}}, \delta_{\mathrm{cr}}$ corresponding to $\theta_{\mathrm{cr} . \mathrm{a}}$ and $\theta_{\mathrm{cr}}$. w were calculated as well as the ratio of these temperatures for different Biot numbers. The results are shown in Fig. 1. When $\mathrm{Bi} \rightarrow \infty$ (first-order boundary condition), critical values given in [10] are obtained, i.e., $\delta_{\mathrm{cr}}=2.0$ and temperature on the pipe axis $\theta_{\text {cr. }}=1.3862$. The graphs show that with increase in the Biot number, the temperature of the pipe axis increases slowly and the temperature of the pipe wall decreases; the ratio of these temperatures therefore increases appreciably. This is associated with the increase in the permissible $\delta$ when the intensity of heat transfer increases, i.e., for high heat-transfer coefficients there is no reduction in the stability of the process even with large temperature differences between the axis and wall of the pipe.

For common reactors the variation in the Biot number lies in the range $\mathrm{Bi}=1-4$. Corresponding values of the roots of Eq. (8) are given in Table 1. The dependences of $\theta$ on $\rho$ for $\mathrm{Bi}=0-4$ and various values of the heat generation parameter $\delta$ are given in Fig. 2. Analysis showed the presence of large temperature drops along the pipe radius. With increase in the intensity of heat transfer (Bi) these drops

TABLE 1. Roots of Characteristic Equation (18)

| Bi | $\delta$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 0,2 | 0,4 | 0,6 | 0,8 | 1,0 | 1,2 |
| 1,0 | 0,029488 | 0,073975 | - | - | - | - |
| 2,0 | 0,027800 | 0,063280 | 0,11252 | 0,19560 | - | - |
| 3,0 | 0,027283 | 0,060465 | 0,10142 | 0,16109 | 0,25651 | - |
| 4,0 | 0,027033 | 0,059175 | 0,097853 | 0,14879 | 0,22269 | 0,35355 |



Fig. 2. Temperature distribution over tube section: a) $\mathrm{Bi}=1.0$; b) 2.0 ; c) 3.0 ; d) 4.0.
decrease at constant values of the parameter $\delta$. There is also a corresponding drop in absolute temperatures over the whole section of the pipe. To determine the permissible radius of the pipe, the value $r_{0}$ can be eliminated from the expression for $\delta$ and Bi . The corresponding relation of $\delta$ to Bi takes the form:

$$
\begin{equation*}
\delta=C \mathrm{Bi}^{2}, \tag{10}
\end{equation*}
$$

where

$$
C=h E k \lambda_{\text {eff.r }} R T_{\mathrm{m}}^{2} \alpha^{2}
$$

Calculation of dependences of $\delta$ on Bi allows the determination of the intersection of the curves $\delta=\delta(\mathrm{Bi})$ and $\delta_{\mathrm{cr}}=\delta_{\mathrm{cr}}(\mathrm{Bi})$, and hence the corresponding values of Bi , from which the maximum permissible pipe radius can be found.

As an example take the calculation of the permissible pipe radius for the synthesis of higher aliphatic compounds from the oxidation of hydrocarbons. This process can be carried out in several ways. Consider the case in which the pipes are packed with catalyst and the external coolant is at constant temperature around the pipes. Because of the small fractional conversion of the reactants per pass through the reactor, the rate of reaction is dependent only on the temperature and does not depend on the extent of conversion, i.e., a first-order reaction [11].

The parameters are [11]:

$$
\begin{gathered}
E=104500 \mathrm{~J} / \mathrm{mole} \quad R=8.36 \mathrm{~J} / \mathrm{mole} \\
T_{\mathrm{m}}=423^{\circ} \mathrm{K} ; \alpha=394 \quad \mathrm{~W} / \mathrm{m}^{2} \cdot \mathrm{deg} .
\end{gathered}
$$

The value of $\lambda_{\text {eff. }}$ r was determined as in [12]. $\lambda_{\text {eff. }}=1.98 \mathrm{~W} / \mathrm{m} \cdot \mathrm{deg}$ (for the usual method of reactor operation); corresponding value of $\mathrm{c}=0.26$; from the graph $\mathrm{Bi}=1.75$. Consequently the critical radius of the pipe, $r_{0}=0.0088 \mathrm{~m}$, i.e., the permissible diameter is about 18 mm .

It should be noted that for low Bi , the value $\delta_{\mathrm{cr}}$ decreases and consequently the process becomes unstable at significantly lower heat generation. Obviously for reactions of orders other than zero the process will become more on account of the decrease in concentration, and consequently also the heat generation over the section, at higher temperatures. The value $\delta$ is particularly important when specifying the pipe radius, since $\delta \sim r_{0}^{2}$, which can result in loss of stability for even a small increase in the pipe radius. The effect of the temperature of the medium should also be noted. A small decrease in this temperature can lead to a sharp rise in the parameter $\delta$ and, consequently, disruption of the process.

## NOTATION

[^0]```
\lambdaeff.r is the effective radial thermal conductivity of the granular layer;
\rho=r/ ro
\alpha
E
R
T, Ta, T W, T
k
h
0=E(T- Tm
\delta= hEkrro
```



```
\sigma
Bi}=\alpha\mp@subsup{r}{0}{}/\mp@subsup{\lambda}{\mathrm{ eff. }}{
0a}=E(\mp@subsup{T}{a}{}-\mp@subsup{\textrm{T}}{m}{\prime})/R\mp@subsup{T}{m}{2}
0
\lambdaeff. z
z
wg
\psi
n
is the effective radial thermal conductivity of the granular layer;
is the dimensionless radius;
is the coefficient of heat transfer from the layer to the cooling agent;
is the activation energy of the reaction;
is the universal gas constant;
are the absolute temperature in the cross section, the axial temperature, the
wall temperature, and the temperature of the medium, respectively;
is the preexponent of the reaction rate constant;
is the thermal effect of the reaction;
is the heat-generation parameter;
is the reaction rate constant;
is the root of characteristic equation (8);
is the Biot number;
\(\theta_{a}=E\left(T_{a}-T_{m}\right) / R T_{m}^{2} ;\)
\(\theta_{\mathrm{w}}=\mathrm{E}\left(\mathrm{T}_{\mathrm{w}}-\mathrm{T}_{\mathrm{m}}\right) / R \mathrm{~T}_{\mathrm{m}}^{2}\);
\(\lambda_{\text {eff. } \mathrm{z}}\)
is the effective longitudinal thermal conductivity of the layer;
is the longitudinal coordinate;
are the linear velocity and heat capacity of the gas, respectively;
is the reaction rate;
is the number of reactions.
```

Subscript
cr denotes the value under critical conditions.

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[^0]:    $\mathrm{t}, \mathrm{t}_{\mathrm{w}}, \mathrm{t}_{\mathrm{m}}$ are the temperature, wall temperature, and temperature of the medium, respectively; $Q \quad \mathrm{is}$ the power of heat generation per unit volume;
    $r_{0} \quad$ is the pipe radius;
    r is the flow radius;

