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#### Abstract

The effective thermal conductivity, $k_{E}$, of a packed bed, that was six inches in diameter and 2.5 feet high, of calcium orthophosphate pellets was determined with superheated steam flowing through the bed. The tablet shaped pellets had a psuedo particle diameter of 0.0134 ft . The effective thermal conductivity of the packed bed varied from 0.16 to $1.00 \mathrm{~B} . \mathrm{t} . \mathrm{u} . / \mathrm{hr} . / \mathrm{ft} .^{\circ} \mathrm{F}$. and was found to depend upon the modified Reynolds number in the $548-588^{\circ} \mathrm{F}$. superficial temperature range. However, $k_{E}=0.39$ was independent of the modified Reynolds number in the $673-863^{\circ} \mathrm{F}$. range.


TTERE HAVE BEEN a number of heat transfer studies (1-5) in porous media. However, most of the previous work has been concerned with fluids other than steam. Also, only a limited amount of data has been obtained at elevated temperature levels.

The purpose of this study was to determine, using flowing superheated steam, the effective thermal conductivity of a packed bed of calcium orthophosphate pellets. These values of $k_{\mathrm{E}}$ were studied as a function of the modified Reynolds number.

## THEORETICAL

The packed bed was assumed to be a solid cylinder. The thermal conductivity of this cylinder was equal to the effective thermal conductivity. Under steady state conditions with the fluid heat capacity remaining constant the effective thermal conductivity of a packed bed may be expressed by:

$$
\begin{equation*}
G C_{\mathfrak{p}}\left(\frac{\partial t}{\partial z}\right)=k_{\mathrm{E}}\left[\frac{1}{r}\left(\frac{\partial t}{\partial r}\right)+\frac{\dot{\partial}^{2} t}{\partial r^{2}}\right] \tag{1}
\end{equation*}
$$

Therefore, if both radial and axial temperature distributions for the packed bed are known, the effective thermal conductivity may be evaluated. The values of $k_{\mathrm{E}}$ were obtained, using the differential form of Equation 1.

## EXPERIMENTAL EQUIPMENT AND PROCEDURE

The entire experimental equipment arrangement has been shown in Figure 1. The packed bed, whose void fraction was 0.299 , is shown in more detail in Figure 2. The pellets had a bulk density of 0.55 gram/cc. The packed bed was six inches in diameter and 2.5 feet high. The bed was held fixed by glass beads and wire mesh packing. It was supported at the base by a conical shaped screen. The bed had a jacket, whose inside diameter was eight inches. The jacket contained flowing steam.

Superheated steam at atmospheric pressure entered the top of the apparatus and passed through the packed fixed bed. After adjusting the superheated steam to the desired rate of flow and temperature, the bed was allowed to reach thermal equilibrium. Generally, this required about three to four hours. Once thermal equilibrium was established, radial temperature profiles at one-half inch intervals were obtained across the six inch packed bed. Typical examples of the measured temperature profiles are shown in Figure 3 and Figure 4. The sliding radial temperature probes were enclosed in stainless steel protective sheaths. There were three sliding probes that traversed the bed. They were located at zero, 0.863 , and 1.725 feet, respectively, from the top of the catalyst bed.

The flow rates of the superheated steam were obtained by condensing the steam and measuring the resulting condensate.

## DISCUSSION OF RESULTS

Ten experimental runs were conducted at different superheated steam flow rates and temperatures. These were the only variables that were changed throughout the course of this study. Using Equation 1, radial point values of $k_{\mathrm{E}}$ were calculated at the bed depth of 0.863 feet. These


Figure 1. Experimental equipment arrangement


Figure 2. Detailed diagram of the packed bed
radial point values were area averaged to produce an average effective thermal conductivity, shown in Table I.
Also, presented in Table I are superficial modified Reynolds numbers, $D_{\mathrm{p}} G / \mu$ for each experimental run. Because the calcium orthophosphate particles were cyllinderically shaped, a psuedo particle diameter, $D_{p}$, was determined:

Since:

$$
\begin{equation*}
\psi=\frac{2(H+R)}{R H} \tag{2}
\end{equation*}
$$

and $\psi$ may be defined by:

$$
\begin{equation*}
\psi=\frac{6}{D_{\mathrm{p}}} \tag{3}
\end{equation*}
$$

Substituting $R=0.125$ in and $H=0.094$ in, the value $D_{\mathrm{p}}=0.0134 \mathrm{ft}$. was determined. This value of $D_{\mathrm{p}}$ was used in the determination of each modified Reynolds number. These modified Reynolds numbers were based on the superficial flow conditions above the bed.

> BED HEIGHT (FT) $0 \quad 0.000$ 0 0 $\triangle$$\quad .863$


Figure 3. Radial temperature profiles in packed bed (run 2)


Figure 4. Radial temperature profiles in packed bed (run 10)

|  | Table I. Effective Thermal Conductivity Data |  |  |
| :---: | :---: | :---: | ---: |
| Run Number | Inet Bed <br> Temp., ${ }^{\circ} \mathrm{F}$. | $N_{\mathrm{Re}}$ | $k_{\mathrm{E}}$ |
| 1 | 673 | 84.5 | 0.46 |
| 2 | 674 | 52.7 | 0.42 |
| 3 | 588 | 20.8 | 0.16 |
| 4 | 560 | 41.9 | 0.22 |
| 5 | 863 | 36.8 | 0.42 |
| 6 | 862 | 45.9 | 0.35 |
| 7 | 765 | 64.5 | 0.32 |
| 8 | 676 | 65.5 | 0.37 |
| 9 | 545 | 64.9 | 0.40 |
| 10 | 576 | 89.6 | 1.00 |

Values of $k_{\mathrm{E}}$ at superficial temperatures of $673-863^{\circ} \mathrm{F}$. are plotted in Figure 5 vs . the modified Reynolds number. Lower range Reynolds number runs, e.g., $N_{\mathrm{Re}}=20$, were not obtained due to physical equipment limitations. Within the accuracy of the data at this superficial temperature range, $k_{\mathrm{E}}=0.39$ was independent of the modified Reynolds number. This consistency of $k_{E}$ in Figure 5 was expected. Since all of the profile data were treated in the same manner, it is believed the axial measurements, though widely spaced, were representative of the bed.

Values of $k_{\mathrm{E}}$ at superficial temperatures of $545-588^{\circ} \mathrm{F}$. are plotted in Figure 6 vs. the modified Reynolds number. From Figure 6 it may be seen that $k_{\mathrm{E}}$ varied from 0.16 to 1.00 at this superficial temperature range and was dependent upon the modified Reynolds number. In the lower $N_{\text {Re }}$ region the axial distribution did not appreciably vary with temperature. However, the radial profiles changed more rapidly at the higher temperature level. This was due to the greater driving force, existing between the bed and jacket. This accounted for the difference of $k_{\mathrm{E}}$ values at the lower $N_{\mathrm{Re}}$ range.

At higher $N_{\mathrm{Re}}$ the radial profiles were flattened. This lessened the heat loss in that direction, causing only a moderate difference with temperature. The axial profiles were slightly greater in the lower temperature region. This was due to relatively uniform temperatures in the upper portion of the bed. As the temperature decreased in the lower part of the packed bed, this resulted in a greater axial differential. The profiles at the higher temperatures were great enough to offset the axial decrease through the bed. This distribution interaction explained the higher $k_{\mathrm{E}}$ at $N_{\mathrm{Re}}=89.6$.


Figure 5. Effective thermal conductivity of the packed bed (inlet bed temperature $673^{\circ}$ to $863^{\circ} \mathrm{F}$.)


Figure 6. Effective thermal conductivity of the packed bed (inlet bed temperature $545^{\circ}$ to $588^{\circ} \mathrm{F}$.)

## NOMENCLATURE

$C_{p}=$ heat capacity at constant pressure, [B.t.u. $\left./(\mathrm{lb} . \mathrm{m})\left({ }^{\circ} \mathrm{F}.\right)\right]$
$D_{\mathrm{p}}=$ psuedo particle diameter, ft.
$\mathrm{G}=$ mass flow rate, $\left[\mathrm{lb} ._{\mathrm{m}} /(\mathrm{hr}).\left(\mathrm{ft}^{2}{ }^{2}\right)\right]$
$H=$ particle height, in.
$k_{\mathrm{E}}=$ effective thermal conductivity, [B.t.u./(hr.)(ft.)( $\left.\left.{ }^{\circ} \mathrm{F}.\right)\right]$
$N_{\mathrm{Re}}=$ modified Reynolds number, dimensionless
$R=$ particle radius, in.
$r=$ packed bed radius, ft .
$t=$ temperature, ${ }^{\circ} \mathrm{F}$.
$z=$ packed bed depth from top to bottom, ft.
$\mu=$ viscosity, $[\mathrm{lb} \cdot \mathrm{m} /(\mathrm{hr}).(\mathrm{ft})$.
$\psi=$ (total particle suface/volume of particle), $\mathrm{ft}^{-1}$
ACKNOWLEDGMENT
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# CHO Gas Phase Compositions in Equilibrium with Carbon, and Carbon Deposition Boundaries at One Atmosphere 

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#### Abstract

Gas phase compositions in equilibrium with carbon (graphite) have been calculated for the full composition range of the CHO system and for temperatures in the range of $298^{\circ}$ to $1500^{\circ} \mathrm{K}$., all at atmospheric pressure. The equilibrium gas phase compositions are presented graphically as a function of the $\mathrm{O} / \mathrm{H}$ atom ratio, and are discussed. The species of major importance were found to be $\mathrm{C}, \mathrm{CO}, \mathrm{CO}_{2}, \mathrm{H}_{2}, \mathrm{H}_{2} \mathrm{O}$, and $\mathrm{CH}_{4}$. The species of secondary importance are $\mathrm{C}_{2} \mathrm{H}_{6}, \mathrm{C}_{2} \mathrm{H}_{4}$, and $\mathrm{C}_{2} \mathrm{H}_{2}$, while species such as $\mathrm{CH}_{3} \mathrm{OH}, \mathrm{HCHO}, \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{OH}$, and $\mathrm{C}_{10} \mathrm{H}_{22}$ were found to be present in amounts several orders of magnitude below the amounts of the species of secondary importance. The amount of any trace component can be easily calculated from these data. The carbon deposition boundaries are presented on triangular coordinates and are discussed.


TTHE CHO SYSTEM is of great importance in many areas of modern technology, including fuel cells, combustion, gasification processes, hydrogen production, and chemical synthesis processes ( 8,9 ). As a result, many studies, both experimental $(6,12,14,15,17,18,20,23)$ and theoretical ( $2-4,11,19,22$ ) have been carried out. However, the results on the thermodynamics of the CHO system available in the open literature are of rather limited scope, usually because of the small ranges of the variables covered in specific processes (e.g., hydrocarbon or alcohol synthesis) of interest to those authors. All data available considered together cover but a small fraction of the total possible range of composition included in the CHO system.

This paper considers the CHO gas phase compositions in equilibrium with graphite over the temperature range $298-1500^{\circ} \mathrm{K}$., at a pressure of one atmosphere, for $\mathrm{O} / \mathrm{H}$ atomic ratios from 0.026 to 4.5 , and the carbon deposition boundaries under the same conditions, except over the full range of $\mathrm{O} / \mathrm{H}$ atomic ratios.

## GENERAL THERMODYNAMIC CONSIDERATIONS

Before considering the computational methods, the system and chemical species of interest will be outlined, since they influence the choice of method. The species most likely to be present in the greatest amounts are among those which are most stable under the conditions of interest, i.e., those having the lowest value of the free energy of formation. In the system containing the elements carbon, hydrogen, and oxygen, in the temperature range of $298^{\circ}$ to $1500^{\circ} \mathrm{K}$., and at a pressure of one atmosphere the most stable species are carbon, hydrogen, water, carbon dioxide, carbon monoxide, and methane, with other species such as ethane, methanol, and some of the other hydrocarbons being less stable. In order to perform a completely rigorous set of thermodynamic calculations, it would be necessary to consider every possible species containing the elements $\mathrm{C}, \mathrm{H}$, and O . The elimination of the very large number of high molecular weight species and their isomers

