Chemical Reaction Engineering Aspects of a Rotary Reactor for Carbothermal Synthesis of SiC

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Abstract

Heat transfer in a rotary reactor is described for a reactor consisting of a graphite tube with graphite heating elements, and operating at temperatures between 1773 and 2273 K. Under those conditions heat transfer is very good due to radiation and the high thermal conductivity of graphite. An overall coefficient of heat transfer of at least 400 W/m²K is estimated. As an example of the application of a rotary reactor the carbothermal production of SiC is described. A general conclusion is that rotary reactors are well suited for the endothermal reactions.

1 Introduction

Pure, submicron SiC powder can be produced from SiO₂ and C on a small scale. However, on a larger scale considerable problems are encountered, the selection of the type and design of reactor being poorly described in literature. The moving bed reactor and the rotary reactor have attracted most attention. The application of a simple moving bed reactor with indirect heating is limited to reactors with relatively small diameters. The inner diameter of such reactors is usually smaller than 150 mm due to poor heat transfer. Part of the chemical reaction engineering of a simple, indirectly heated moving bed reactor is described in the literature. We discuss here the chemical reaction engineering aspects of a rotary reactor applied to the carbothermal production of SiC from silica and carbon. We will also describe some experimental results obtained with such a reactor.

2 Reactor Engineering Aspects of Carbothermal Production of SiC

2.1 The carbothermal reaction

The formation of SiC is described by the overall reaction

\[ \text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO} \]

1 kg of a silica–carbon mixture will result in 415 g of SiC at 100% conversion. Usually a small carbon excess is used. Above a temperature of 1510°C the...
partial CO pressure is higher than 1 bar \(10^5\) Pa and, when the reaction takes place at 1 bar total pressure, the CO is forced out of the granules, the bed and the reactor. Under such conditions a reaction rate controlled by gas diffusion or mass transfer is not expected. The reaction is endothermic, with a reaction enthalpy of 604 kJ/mol SiC.

The reaction involves nucleation and growth of SiC particles. Two mechanisms for the growth are possible. The first is a direct solid state reaction; the second consists of a solid state reaction followed by a gas–solid reaction and involves the gaseous SiO:

\[
\text{SiO}_2 + C \rightarrow \text{SiO(g)} + \text{CO}
\]

and

\[
\text{SiO(g)} + 2C \rightarrow \text{SiC} + \text{CO}
\]

Although direct solid state diffusion is probably the main mechanism, the formation of SiO is always observed in practice.

The main parameters determining the particle size of SiC are reaction time, temperature, impurities, type of carbon, and the presence of SiC particles which act as nuclei.

Usually \(\beta\)-SiC is obtained. When the reaction is carried out on a laboratory scale with excess silica in a nitrogen atmosphere, \(\alpha\)-SiC is then obtained due to the incorporation of nitrogen in the structure. 7

2.2 The rotary reactor

Rotary reactors are often used for the processing of solids. They have the advantage that the heat transfer is good and that the operation is simple. We can distinguish between directly and indirectly heated reactors. Examples of the first type are rotary reactors used for the production of cement and ferrites. Examples of the second type with a graphite tube are less common, but are found in the production of tungsten carbide and for some other high temperature processes in non-oxidizing atmospheres. 8 Although some authors suggest that the indirectly heated reactors are new, this is certainly not the case. 3 An example of such a reactor for the synthesis of SiC with heating elements inside the tube is described in a Japanese patent. 9 We have applied this type of reactor to the carbothermal synthesis of SiC, using a rotary reactor with a graphite tube and graphite heating elements outside the tube.

The working conditions are the following. The degree of filling is usually 5–25% volume. The ideal movement of the solid particles is shown in Fig. 1.

Typical data are: rotational speed 1–10 rpm, inclination 1–5°, residence time 0.25–3 h and length to diameter ratio about 10. The heated length may be up to 3.5 m. Under the right conditions the bed is radially mixed after 3 rotations. 10 When the rotational speed is too low the movement of the solid is poor and there is insufficient radial mixing. 11 At a high rotational speed the particles are pressed against the wall by the centrifugal force. The residence time in the heated zone can be estimated from eqns (1a) and (1b):

\[
t = KL/(ND \tan \alpha) \quad (1a)
\]

and

\[
t = 4V_t/(\gamma \pi DL) \quad (1b)
\]

Here \(L\) is the length of the heated zone, \(N\) the rotational speed in revolutions per unit time, \(\gamma\) the degree of filling, \(V_t\) the volume flow, \(D\) the inner tube diameter, and \(\alpha\) the angle of inclination. \(K\) is a factor depending on the degree of filling.

Equation (1a) is the mathematical description of the movement of a particle or granule in the heated zone. The displacement in the longitudinal direction of the heated zone is \(D \tan \alpha/K\) per revolution. The dimensionless constant \(K\) is approximately 0.2. Equation (1b) gives the volume flow divided by the volume of the bed in the heated zone.

Under most reaction conditions the residence time distribution can be neglected, i.e. the particles move like in a plug flow. 11 12 In order to prevent segregation the use of a uniform granulate is advised. 13
2.3 Heat transfer

When a reaction is both fast and endothermic, like the carbothermal reaction of SiO₂ with C, it is of importance to have a high heat transfer in order to prevent a reaction rate limited by heat transfer. In this section we consider the heat transfer characteristics of a rotary reactor. To this end we distinguish heat transfer from the heating elements to the tube, heat transfer through the tube and heat transfer from the tube to the bed. These terms contribute to the overall resistance to heat transfer, 1/U, according to

\[ \frac{1}{U} = \frac{R}{\ln(1 + \frac{d}{R})/\lambda + \frac{R}{\alpha_1(R + d)} + 1/\alpha_2} \]  

(2)

\( R \) is the inner radius of the tube, \( d \) the tube thickness, \( \lambda \) the thermal conductivity of the tube, \( \alpha_1 \) the coefficient of heat transfer from the elements to the outer tube surface, and \( \alpha_2 \) is the coefficient of heat transfer from the inner tube surface to the bed.

Both conduction, convection and radiation will be taken into account. Heat losses, e.g. axial heat losses from the tube, or losses through the insulation, etc. are not considered however. The heat produced by the elements is consumed by heating up the SiO₂/C granules and by the reaction only.

For the reaction zone we can write

\[ U_1 A_1 \Delta T = HV \]  

(3)

where \( A_1 \) is the surface through which the heat is transported, \( \Delta T \) the temperature difference between the heating elements and the bed, \( V \) the volume of the bed in the reaction zone and \( H \) the reaction enthalpy per unit volume and per unit time. When \( L_1 \) is the length of the reaction zone and \( \gamma \) the degree of filling, we have \( A_1 = 2\pi R L_1 \) and \( V = \pi R^2 L_1 \).

For the zone where the granulate is heated eqn (4) holds

\[ FC_p dT_1 = dA_2 U_2(T_0 - T_1) \]  

(4)

\( F \) is the mass flow, \( C_p \) the specific heat, \( dA_2 \) the surface through which the heat is transported, \( (T_0 - T_1) \) the temperature difference between the elements and the bed and \( dT_1 \) the temperature increase of the bed. This equation indicates that the energy which is transferred from the heating elements to the bed is used entirely to heat up the granules or particles which enter the heated zone. It takes time to heat up the granules; this heating time is equivalent to the distance travelled by the granules before they are heated up. Then \( dL_2 \) is the length of the zone where the material is heated to, say, 97% of the reaction temperature we have

\[ dA_2 = 2\pi R dL_2 \]  

(5)

We shall subsequently describe the three contributions to U.

2.3.1 Heat transfer from the elements to the tube

The coefficient of heat transfer from the elements to the outside of the tube, \( \alpha_1 \), can be written as

\[ \alpha_1 = \alpha_{\text{cond}} + \alpha_{\text{conv}} + \alpha_{\text{rad}} \]

The conduction term can be calculated from the thermal conductivity, \( \lambda \), and the distance \( x \) between the tube and the elements: \( \alpha_{\text{cond}} = \frac{\lambda}{x} \). Table 1 gives conductivity values for some gases. For \( x \geq 0.05 \text{ m} \) one gets \( \alpha_{\text{cond}} \leq 2.5 \text{ W/m} \text{K} \). This is a relatively small value and we will see that this term can be neglected in our calculations.

The coefficient of heat transfer due to convection can be calculated from the Nusselt number, \( N_u \),

\[ N_u = 0.55 \left( \frac{P_r G_r}{R} \right)^{1/4} \]  

(6)

Here the Prandtl number \( P_r \) is only weakly temperature dependent and is 0.68 for \( N_2 \) and CO and 0.53 for Ar. \( G_r \), the Grashof number can be calculated from eqn (7)

\[ G_r = \frac{AQ g h^3}{\mu^2} \]  

(7)

\( Q \) is the density of the gas when at the heating element temperature, \( \Delta Q \) the difference in density of the gas at the tube and at the elements, \( \mu \) the dynamic viscosity, \( g \) the gravitational constant and \( h \) the outside tube diameter. Table 2 gives some physical data of the relevant gases and Table 3 gives data for \( \alpha_{\text{conv}} \) as a function of the tube diameter and the temperature difference. The average temperature is taken at 2073 K. From Table 3 it can be seen that the value for \( \alpha_{\text{conv}} \) is maximally 6 W/m²K. As we have heat transfer from the elements to the gas and from the gas to the tube \( \alpha_{\text{conv}} = \frac{1}{2} \alpha_{\text{conv}} \), which is less than 3 W/m²K.

Table 1. The thermal conductivity of Ar, CO and \( N_2 \) in W/mK

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Gas</th>
<th>( \lambda ) (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>Ar</td>
<td>0.017</td>
</tr>
<tr>
<td>2073</td>
<td>CO</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>( N_2 )</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Table 2. The dynamic viscosity \( \mu \) and the density \( Q \) for three gases at 2073 K.

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \mu ) (Ns/m²)</th>
<th>( Q ) (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>( 6.5 \times 10^{-6} )</td>
<td>0.165</td>
</tr>
<tr>
<td>CO</td>
<td>( 6.7 \times 10^{-6} )</td>
<td>0.165</td>
</tr>
<tr>
<td>Ar</td>
<td>( 8.5 \times 10^{-6} )</td>
<td>0.235</td>
</tr>
</tbody>
</table>
Finally we estimate the contribution of radiation to the heat transfer from the elements to the tube. Here we use the well known expression\(^\text{14,15}\)

\[
\alpha_{\text{rad}} = \left( \frac{T_1}{100} \right)^4 - \left( \frac{T_2}{100} \right)^4 \frac{C_{12}}{(T_1 - T_2)} \quad (W/m^2K) \quad (8)
\]

Here \(T_1\) is the temperature of the elements, \(T_2\) is the temperature of the outer tube surface. The radiation factor \(C_{12}\) can be calculated from eqn (9)

\[
C_{12} = \frac{5.67 \times 10^{-8}}{\left[ 1/e + F_2/(F_1/e - 1) \right]} \quad (W/m^2K^4) \quad (9)
\]

When both the elements and the tube are made of graphite the emissivity coefficient \(e\) is about 0.9. \(F_2\) is the surface area of the tube in the heated zone, \(F_2 = 2\pi (R + d) L\), \(F_1\) is the surface area of the elements and it also accounts for the heating of the outer tube surface by reflection from the insulation. For our calculation we take \(F_1\) as a cylinder with surface \(2\pi (R + d + x) L\), \(x\) being the distance between the tube and elements/insulation. In Table 4 values for \(C_{12}\) are given as a function of \(x\) and the outside tube diameter. From this table we can see that \(C_{12}\) decreases with \(x\), but is approximately equal to 4.0.

In Table 5 we show \(\alpha_{\text{rad}}\) for different values of \(T_1\) and \(T_2\). From these data it is evident that \(\alpha_{\text{rad}}\) is much larger than \(\alpha_{\text{conv}}\) and \(\alpha_{\text{cond}}\). It can also be seen that \(\alpha_{\text{rad}}\) is large when the difference \(T_1 - T_2\) is small or when \(T_1\) is high.

From these calculations we conclude that heat transfer from the heating elements to the tube is dominated by radiation and that both conduction and convection can be neglected. The value for \(\alpha_1\) is estimated to be 1000–1800 W/m²·K.

### Table 4. The influence of the tube-element distance \(x\) and the outer tube diameter on \(C_{12}\), with emissivity \(e = 0.9\)

<table>
<thead>
<tr>
<th>(x) (m)</th>
<th>Outer tube diameter (m)</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>4.26</td>
<td>4.51</td>
<td>4.57</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>3.93</td>
<td>4.38</td>
<td>4.49</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>3.41</td>
<td>4.15</td>
<td>4.33</td>
<td></td>
</tr>
</tbody>
</table>

\(\alpha_{\text{wb}} = 6\lambda_b/(2R)\) \quad (10)

\(\lambda_b\) is the thermal conductivity of the bed; it depends on the temperature and on the size of the granulate, \(d_p\).\(^6\) At 1973 K one has for a granulate with \(d_p = 1\) mm \(\lambda_b = 1.5\) W/mK, for \(d_p = 5\) mm \(\lambda_b = 5\) W/mK and for \(d_p = 10\) mm \(\lambda_b = 8\) W/mK. Table 7 gives...
values of $\alpha_{wbc}$ as a function of $R$ and $d_p$. These values only hold for the part of the tube where the granulate is in contact with the tube.

For the instationary model, to describe heat transfer from the inner tube surface to the bed by contact, the Higbie penetration theory can be used.\(^4\) Lehmberg et al. showed that the penetration theory should be corrected for film resistance near the inner surface.\(^10\) At low temperatures, when radiation can be neglected, this correction leads to a lower value of $\alpha_{wbc}$. In this regime the influence of the granulate size on $\alpha$ is explained by an increase of the film thickness with increasing $d_p$. This results in a decrease of $\alpha_{wbc}$. At high temperatures radiation becomes important, film resistance becoming relatively less important and so the bed may be considered as a continuum. As far as the contribution of radiation to $\alpha_{wbc}$ is concerned the penetration theory seems applicable.

\[ \alpha_{wbc} = \frac{(T_3/100)^4 - (T_4/100)^4}{C_{12}/(T_3 - T_4)} \]  
\[ (W/m^2K) \]  
\[ C_{12} = 5.67/(1/e^2 + F_3/F_4(1/e^4 - 1)) \]  
\[ (W/m^2K^4) \]  
\[ e_3 \text{ and } e_4 \text{ are the coefficients of emissivity for the tube and bed, both are about 0.9, } F_3 \text{ is the tube surface in contact with the gas phase, } F_4 \text{ the upper surface of the bed, } T_3 \text{ is the temperature of the inner tube surface and } T_4 \text{ of the upper surface of the bed.} \]

In Table 5 values of $\alpha_{wbc}$ are given for several values of $T_3$ and $T_4$. From this table it can be seen that $\alpha_{wbc}$ is quite large.

Separate heating of the upper surface of the bed is not accounted for. The heating of the upper surface of the bed is compensated by the higher energy consumption which is due to a higher reaction rate. The residence time of the granulate at the upper surface of the bed is of the order of magnitude of a few seconds, which is relatively short. So, a uniform temperature of the bed is assumed.

Heat transfer by convection between the tube and the gas phase and between the gas phase and the bed is described in literature.\(^18\) It is assumed that the heat transfer by forced convection from the tube to the bed is less than 6 W/m\(^2\)K. A similar calculation as given in section 2.3.1 shows that the contribution by convection is also very small. This means that again the contributions of conduction and convection can be neglected compared to radiation.

We can now calculate $\alpha_2$ from

\[ \alpha_2 = 0.7\alpha_{wbc} + 0.3\alpha_{wbc} \]  
\[ (14) \]

A conservative estimation gives a value of 1000 W/m\(^2\)K for $\alpha_2$.

### 2.4 The overall coefficient of heat transfer

By application of eqn (2) the overall coefficient for heat transfer can be estimated. Table 8 gives data for $U$ as a function of $R$ and $d$, assuming

Table 8. The overall coefficient of heat transfer $U$ in W/m\(^2\)K, as a function of the inner tube diameter $2R$ and the thickness $d$ of the tube

<table>
<thead>
<tr>
<th>$d$ (m)</th>
<th>2$R$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>0.01</td>
<td>510</td>
</tr>
<tr>
<td>0.03</td>
<td>400</td>
</tr>
</tbody>
</table>
\[ \alpha_1 = 1300 \text{ W/m}^2\text{K}, \quad \alpha_2 = 1000 \text{ W/m}^2\text{K}, \quad \text{and} \quad \lambda = 30 \text{ W/m}^2\text{K}. \] From the table we conclude that a value of \( U = 400 \text{ W/m}^2\text{K} \) is a conservative estimation. This is a relatively high value, which is due to the large radiation contribution and the high thermal conductivity of graphite.

3 Experimental Results

We have performed a series of experiments to verify that a rotary reactor can be used for the production of SiC. Since solid state diffusion is important in our case for the formation of SiC the particle sizes of both silica and carbon have to be small and they have to be well mixed. Table 9 gives the analysis of the starting powders. An experimental, precipitated silica with properties similar to Aerosil ox 50 was used. The powders with a mole ratio of 1:3 were wet mixed in an attritor for 45 min, using SiC balls of 3 mm diameter. Nuclei were added prior to milling. The use of an organic liquid instead of water results in a higher chemical reaction rate, probably due to improved mixing and milling. After attrition milling the mixture is dried and granulated. Figure 2

**Table 9. Analysis of silica and carbon black**

<table>
<thead>
<tr>
<th>Type</th>
<th>( \text{SiO}_2 ) (Aerosil ox 50)</th>
<th>( \text{Carbon (Printex U)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface (m(^2)/g)</td>
<td>50</td>
<td>110</td>
</tr>
<tr>
<td>Metal content (% wt)</td>
<td>&lt;0.05</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Volatile matter (% wt)</td>
<td>&lt;1</td>
<td>&lt;6</td>
</tr>
<tr>
<td>Moisture (% wt)</td>
<td>&lt;1.5</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Density (g/l)</td>
<td>--</td>
<td>410 (pearls)</td>
</tr>
</tbody>
</table>

*Raw materials: Degussa, Frankfurt, FRG.*

Fig. 2. Optical micrograph of a precipitated silica–carbon black mixture after attrition milling. Bar length 20 \( \mu \)m. The white particles are silica, the black particles are carbon black.

Fig. 3. Thermogravimetric analysis of the carbothermic synthesis of SiC. Region 1–2 indicates the heating of the pellets, 2–3 is the isothermal part (i.e. 15 min at 1600°C), 3 indicates the cooling range.
Engineering aspects of a rotary reactor for carbothermal synthesis

shows an optical micrograph of the mixed powder. Each type of reactor requires a granulate with a specific size and strength. For our experiments with a rotary reactor, we used tablets with a diameter and height of 5 mm and a density of 1.1 g/ml.

First some experiments were carried out in a thermobalance (Netzsch STA 429). The tablets were heated in an alumina crucible at a rate of 20 K/min. The alumina reacts slightly with the tablets, but this does not influence the present results. As shown in Fig. 3 volatile matter is lost between 100 and 100°C. At about 1200°C the reaction starts. At 1600°C, in flowing helium, the reaction time is usually less than 10 min. This shows that the carbothermal synthesis of SiC is fast indeed. Some SiO deposits at the outlet of the thermobalance.

The next experiments were performed in a rotary reactor with a heated length of 1.6 m and an inner tube diameter of 0.1 m. Both the reactor tube and the heating elements were made of graphite. Both ends of the tube were water cooled. The reactor was purged with 1 m³ nitrogen per hour. The tablets were fed through a lock by a vibrating feeder, and were removed from the reactor through a lock. The rotation speed was 3 rpm, the angle of inclination 2°. Further reaction conditions were: inner tube temperature 1850°C (determined by pyrometry), feed 2.0 kg/h, degree of fill about 20% vol., residence time in the heated zone about 30 min. Under these conditions 0.9 kg/h of reaction product were obtained. Runs normally lasted 9 h. The product contained maximal 10% free carbon and less than 0.5% wt of oxygen. No dust problems were encountered.

4 Discussion and Conclusion

According to eqn (3) with $U = 400 \text{ W/m}^2\text{K}$, $\gamma = 0.2$, $H = 1600 \text{ kJ/m}^2\text{s}$ and a reaction time of 30 min, the temperature difference between the heating elements and the bed is estimated to be $\Delta T = 20 \text{ K}$ for the reactor used. The experiments showed that the carbothermal reaction runs smoothly under these conditions. It should be possible to use rotary reactors with inner diameters larger than 0.1 m, increase the degree of fill and decrease the residence time. The temperature difference $\Delta T$ increases in proportion to the tube diameter. This limits the diameter to about 0.4 m. According to eqn (4) with $U = 400 \text{ W/m}^2\text{K}$ and $C_p = 1570 \text{ J/kg K}$, the tablets were heated up after 30 mm. So, from this point of view also, a larger rotary reactor seems possible. As mentioned before, heat losses were not considered here. Cautiously, one may say that the rotary reactor seems attractive for all carbothermal reactions where CO is forced out of the granulate and out of the bed, like in the production of SiC, TiC, and others.

References

16. Documentation 'Syngraphorm' Signi Elektrographit GmbH, Meitingen, FRG.