Modeling and control of size distribution for fluidized bed silane decomposition

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Photovoltaic Industry

Industry Growth
IEA-PVPS, ’03

Solar Cell Production

Metallurgical Grade $3-5 per kg
Electronic Grade $40-60 per kg

Raw Material
SiHCl₃ (TCS) Distillation
Decomposition
Crystallization
Wafers
IC’s

Missing Link
Insufficient

Solar Grade Aim: $20 per kg
Remelt/Cryst
Wafers
PV Cells
Silicon Production

Siemens Reactor
Batch Process
1100°C

Fluid Bed Reactor
Continuous Process
650°C
Large surface area

Dense Phase
SiH₄ Decomposition
Particle Growth
Size Distribution

SiHCl₃ or SiH₄

SiH₄ Decomposition
Modeling Particulate Processes

Crystallization
Aerosol Formation
Cell Growth
Fluidization

Population Balance

$$V \left( \frac{\partial n}{\partial t} + \nabla \cdot \mathbf{v}_i n + D - B \right) + n \frac{dV}{dt} = - \sum_k Q_k n_k$$

- Density distribution
- Internal flux
- Death and birth terms

Continuous phase
Distributed phase
External coordinates
Space, time
Internal coordinates
Size, age, composition
External flow terms
Overall Reaction and Gas Phase

Thermal Decomposition of Silane: $\text{SiH}_4(g) \rightarrow \text{Si}(s) + 2\text{H}_2(g)$

Ideal operation: dense zone is a CSTR

Gas phase balance equations ($\text{SiH}_4$, $\text{H}_2$)

$$\frac{d(V_g \cdot C_{so})}{dt} = F_{in} \cdot C_{si} - F_{out} \cdot C_{so} - (R + \text{loss}_{\text{hom}}) \cdot V_g$$

$$\frac{d(V_g \cdot C_{ho})}{dt} = -F_{out} \cdot C_{ho} + 2 \cdot (R + \text{loss}_{\text{hom}}) \cdot V_g$$

Reaction rate defined by Lai et al. (1986)

$$R_{\text{het}} = 2.79 \times 10^8 \exp(-19530/T)C_s$$

$$R_{\text{hom}} = 2 \times 10^{13} \exp(-26000/T)C_s$$

Accounting for loss through entrainment $\rightarrow$ Total reaction:

$$R = R_{\text{het}} + (1 - \eta)R_{\text{hom}}$$

$\eta$ is fraction of product (powder) lost

Behavior along external coordinate axes: position and time
Solid Phase

Size interval mass balance

\[ \frac{dM_i}{dt} = f_{i-1} + rxn_i - f_i + f_{a_i^{IN}} - f_{a_i^{OUT}} + \sum_i q_i \]

Assume

\[ rxn_i = R \cdot \frac{A_i}{\sum_i A_i} \]

\[ f_{a_{i,j}} = k_{i,j} C_i C_j \Rightarrow \]

\[ f_{a_i^{OUT}} = \sum_j \left( f_{a_{i,j}} \cdot \frac{m_i}{m_i + m_j} \right) \]

\[ f_{a_i^{IN}} = \sum_j \sum_k f_{a_{j,k}}, \text{ for} \]

\[ m_i^{LB} \leq (m_j + m_k) < m_{i+1}^{LB} \]

Derive \( f_i \)

assuming continuous number:

\[ N_i = \frac{M_i}{m_i} \Rightarrow \frac{dN_i}{dt} = \frac{1}{m_i} \cdot \frac{dM_i}{dt} \]

can obtain:

\[ f_i = (rxn_i + a\text{term}_i) \cdot \frac{m_i+1}{m_{i+1} - m_i} \]

\[ a\text{term}_i = f_{a_i^{IN}} - m_i N_i \]

Behavior along internal coordinate axis: size
Solution Strategy for Discrete Model

Ordinary differential equations for mass in gas and solid phases + Algebraic constitutive equations

DAE system solved by MATLAB’s ode15s

<table>
<thead>
<tr>
<th>Adjustable Parameters</th>
<th>Example Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>Fraction of powder lost</td>
</tr>
<tr>
<td>$k_{i,j}$</td>
<td>Aggregation proportionality constant</td>
</tr>
</tbody>
</table>
Experimental Data for Validation

**Operation of pilot scale reactor**

- Load known initial distribution
  - sieves used to measure distribution

- Continuous feed to fluidized bed

- Withdraw samples regularly
  - ~8-12 samples per run
Particle Size Distribution
Controlling Continuous Operation

**Objective**
control: mass of silicon
manipulate: external flow rates

\[ \sum_i M_i - \sum_i q_i \]

- **Si powder**
- **H\(_2\)**
- **Si seed**
- **Si product**
- **SiH\(_4\)**
- **H\(_2\)**
- **feed**

System
Controller
Inventory Control of Population Balance

\[
\frac{dM_i}{dt} = f_{i-1} + rxn_i - f_i + f_{a_i}^{IN} - f_{a_i}^{OUT} + \sum_i q_i
\]

\[
g_i
\]

Apply inventory control to system:

\[
\sum_i \frac{dM_i}{dt} = \sum_i g_i + \sum_i q_i = -K \left( \sum_i M_i - M^* \right)
\]

\[
\Rightarrow \sum_i q_i = -\sum_i g_i - K \left( \sum_i M_i - M^* \right)
\]

Constant mass in reactor: \(product = -\sum_{i=1}^{N} g_i - K \left( \sum_{i=1}^{N} M_i - M^* \right)\)

Constant seed mass: \(seed = -\sum_{i=1}^{I_s} g_i - K \left( \sum_{i=1}^{I_s} M_i - M_s^* \right)\)
Response to Set Point Changes

- Total Mass in Reactor
- Product Flow
- Seed Mass in Reactor
- Seed Flow
System Dynamics

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**Graph 1:**
- **Y-axis:** Product Flow
- **X-axis:** Time (hr)
- **Legend:** Product Flow

**Graph 2:**
- **Y-axis:** Product Average Size (mm)
- **X-axis:** Time (hr)
- **Legend:** Product Average Size

**Graph 3:**
- **Y-axis:** Product Average Size (mm)
- **X-axis:** Seed Mass/Total Mass
- **Legend:** Product Average Size
Silicon Size Distribution

![Graphs showing silicon size distribution](image)
Summary

• Size interval mass balance predictions of particle distribution compare well with data

• Simulations of continuous operation and inventory control indicate that size is controllable

• Further investigate measurability and stability

• Application to other particulate processes or multiscale modeling is significant
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