Determination of Langmuir-Hinshelwood gasification kinetics from integral drop tube experiments

Florian Keller, Felix Küster, Bernd Meyer
I. Motivation & Background
II. Gasification experiments
III. Description of gasification reactivity
IV. Determination of gasification kinetics
V. Summary & Outlook
I. Motivation & Background

Project ibi

Central German lignite

- Production
- Processing
- Extraction
- LT-Conversion
- HT-Conversion

- Montan wax
- Olefins
- Syngas
II. Gasification experiments

Gasification equipment

GMEQ

- Gasification Measurement Equipment
- Drop tube furnace reactor
- $L_{\text{heated}} = 1.75 \text{ m}$
- $T_{\text{max}} = 1300 \degree \text{C}$
- $p_{\text{max}} = 6 \text{ bar}$
- $m_{\text{char, max}} = 1.2 \text{ kg/h}$
- for CO$_2$ and steam gasification
II. Gasification experiments

Gasification equipment
II. Gasification experiments

Experiment overview

<table>
<thead>
<tr>
<th>Char preparation</th>
<th>Gasification experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Central German Lignite</td>
<td>• 66 experiments</td>
</tr>
<tr>
<td>• Pyrolysis in rotary kiln at 600 °C</td>
<td>• Mixtures of steam, CO₂, CO, H₂</td>
</tr>
<tr>
<td>• Crushed to particle size below 200 µm</td>
<td>• 6 bar total pressure</td>
</tr>
<tr>
<td></td>
<td>• 900 to 1100 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>p_{CO₂}</th>
<th>p_{H₂O}</th>
<th>p_{CO}</th>
<th>p_{H₂}</th>
<th>V_{gas}</th>
<th>X_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bar]</td>
<td>[bar]</td>
<td>[bar]</td>
<td>[bar]</td>
<td>[l(STP)/h]</td>
<td>-</td>
</tr>
<tr>
<td>min</td>
<td>0.00</td>
<td>0.00</td>
<td>0.27</td>
<td>0.26</td>
<td>246</td>
</tr>
<tr>
<td>max</td>
<td>3.74</td>
<td>3.91</td>
<td>1.77</td>
<td>1.61</td>
<td>543</td>
</tr>
</tbody>
</table>
III. Description of gasification reactivity

Reaction gas composition

- Reaction gas composition
  - Reactant gas partial pressure
  - Surface saturation (CO$_2$, steam)
  - Inhibition (CO, H$_2$)
→ Langmuir-Hinshelwood rate equation

\[
\frac{dX_C}{dt} = r_{LH} \text{ RPM } \eta
\]

**LH rate expression without inhibition$^1$**

\[
r_{LH} = \frac{k_{11}p_{CO_2}}{1 + k_{12}p_{CO_2}} + \frac{k_{21}p_{H_2O}}{1 + k_{22}p_{H_2O}}
\]

**LH expression of shared active sites$^2$**

\[
r_{LH} = \frac{k_{11}p_{CO_2} + k_{21}p_{H_2O}}{1 + k_{12}p_{CO_2} + k_{13}p_{CO} + k_{22}p_{H_2O} + k_{23}p_{H_2}}
\]

**LH expression of separated active sites$^2$**

\[
r_{LH} = \frac{k_{11}p_{CO_2}}{1 + k_{12}p_{CO_2} + k_{13}p_{CO}} + \frac{k_{21}p_{H_2O}}{1 + k_{22}p_{H_2O} + k_{23}p_{H_2}}
\]

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III. Description of gasification reactivity

Particle structure change

- Reaction gas composition
  → *Langmuir-Hinshelwood rate equation*

- **Particle structure change**
  - Initial increase of reactive surface area
  → *Random Pore model*

\[
\frac{dX_C}{dt} = r_{LH} \ RPM \ \eta
\]

---

**Random Pore Model**

\[
RPM = (1 - X_C)\sqrt{1 - \Psi \ ln(1 - X_C)}
\]

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III. Description of gasification reactivity

Pore diffusion

- Reaction gas composition
  → *Langmuir-Hinshelwood rate equation*

- Particle structure change
  → *Random Pore model*

- **Pore diffusion**
  - Reaction rate limitation at higher temperatures
  → *Pore Effectiveness Factor*

\[
\frac{dX_C}{dt} = r_{LH} \, RPM \, \eta
\]

**Pore Effectiveness Factor**

\[
\eta = \frac{1}{\phi} \left( \frac{1}{\tanh(3\phi)} - \frac{1}{3\phi} \right)
\]

**Thiele modulus**

\[
\phi = L_p \frac{r(C_{As})}{\sqrt{2}} \left[ \int_0^{C_{As}} D_e(\alpha) \, r(\alpha) \, d\alpha \right]^{-\frac{1}{2}}
\]

\[
\phi = L_p \sqrt{\frac{m_{\text{char},0} x_{\text{char},0} R T}{\dot{V}_{\text{Gas}}} \frac{1}{M_c} \frac{1}{2D_e A}} \sqrt{\frac{k_{11}}{1 + k_{12}p_{CO2} + k_{13}p_{CO}}} \frac{1}{k_{12}p_{CO2} - (1 + k_{13}p_{CO}) \ln(1 + k_{12}p_{CO2} + k_{13}p_{CO})}
\]

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Advantages of drop tube furnace experiments

• Single particle behavior

Problems for determination of kinetic expressions

• Linear regression not possible
  – Changing gas composition
  – CO₂ and steam gasification
• Impact of gas phase reaction on gas composition

→ Fitting concept

• Modeling of gasification process
• Determination of deviation between model and experiments
• Minimization of deviation by adjustment of kinetic parameters
IV. Determination of gasification kinetics

Considered reactions

- Heterogeneous water gas reaction
  \[ C_f + H_2O \rightarrow CO + H_2 \]

- Boudouard reaction
  \[ C_f + CO_2 \rightarrow 2 CO \]

- Homogeneous water gas reactions
  \[ CO + H_2O \rightarrow CO_2 + H_2 \]
  \[ CO_2 + H_2 \rightarrow CO + H_2O \]
### Isothermal 1D plug flow gasification model

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
<th>Reaction Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times \frac{dX_{C,i}}{dt}$</td>
<td>Langmuir-Hinshelwood model</td>
<td>(CO$_2$, H$_2$O)</td>
</tr>
<tr>
<td>$4 \times \frac{dn_i}{dt}$</td>
<td>Heterogeneous gasification reactions</td>
<td>(CO$_2$, CO, H$_2$O, H$_2$)</td>
</tr>
<tr>
<td>$1 \times \frac{dl}{dt}$</td>
<td>Gas velocity</td>
<td></td>
</tr>
<tr>
<td>$2 \times \eta_i$</td>
<td>Thiele modulus approach</td>
<td>(CO$_2$, H$_2$O)</td>
</tr>
</tbody>
</table>

→ **Differential algebraic equation system with 9 equations and 14 kinetic constants**
  - Solved in MATLAB
  - Initial condition: experimental conditions
  - Termination criterion: length of reaction tube
IV. Determination of gasification kinetics

Example model course

<table>
<thead>
<tr>
<th>CO₂</th>
<th>CO</th>
<th>H₂O</th>
<th>H₂</th>
<th>Ar</th>
<th>N₂</th>
<th>Initial gas flow [l (STP) /h]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.10</td>
<td>1.12</td>
<td>1.15</td>
<td>0.34</td>
<td>0.33</td>
<td>0.96</td>
<td>507.4</td>
<td>1100</td>
</tr>
</tbody>
</table>

**Reaction gas partial pressure [bar]**

**Initial gas flow [l (STP) /h]**

**Temperature [°C]**

**Gas vol. fraction / carbon conversion X_c**

**Total gas volume flow [l(STP)/h]**

**Reactor length [m]**

**Gas flow**
IV. Determination of gasification kinetics

Fitting procedure

- Experimental results
- Design (14 constants)
- Validation of Effectiveness Factor
- Gasification Model (MATLAB) for 66 experiments
- Average deviation (CO₂, CO, H₂)
- Optimization Algorithm (ModeFRONTIER)
- Optimized Design
Optimization results

→ Kinetic expression: LH with inhibition > LH without inhibition > n-th order
→ Concept of active carbon site competition has no significant effect
→ Effectiveness factor does not improve fitting quality

\[
\frac{dX_C}{dt} = (1 - X_C) \sqrt{1 - \psi} \ln(1 - X_C) \frac{k_{11}p_{CO_2} + k_{21}p_{H_2O}}{1 + k_{12}p_{CO_2} + k_{13}p_{CO} + k_{22}p_{H_2O} + k_{23}p_{H_2}}
\]

<table>
<thead>
<tr>
<th>Relative mole flow deviation</th>
<th>CO\textsubscript{2}</th>
<th>H\textsubscript{2}</th>
<th>CO</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>16,6%</td>
<td>18,4%</td>
<td>7,5%</td>
<td>4,4%</td>
<td></td>
</tr>
</tbody>
</table>
IV. Determination of gasification kinetics

Results

- Carbon conversion $X_C$
- Vol.-fraction CO
- Vol.-fraction H$_2$
- Vol.-fraction CO$_2$

Experiments vs. Simulation at 900 °C, 1000 °C, and 1100 °C.
V. Summary & Outlook

Example model course

Summary
- Gasification experiments with lignite char in PDTF at 6 bar, up to 1100 °C in atmosphere of steam, CO₂, H₂, CO
- Isothermal 1D plug flow gasification model
- Determination of kinetic parameters by model fitting

Outlook
- Comparison of DTF kinetics to TGA derived kinetics
- Method application under more severe reaction conditions
- Integration of methanation reaction, film diffusion
Thank you for your attention!

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