High pressure drop-tube pyrolysis of brown coal and its kinetics

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### Outline

I. Motivation

II. Feedstock characterization

III. Drop-tube reactor and process balancing

IV. Product yields

V. Reaction kinetics

VI. Summary and outlook
High pressure drop-tube pyrolysis

Motivation

Minimized CO₂ emissions

Syngas processing & chemicals synthesis

“Green” H₂ from renewable electricity

Chemical products from domestic carbon resources

Availabilty of domestic lignite

Gasification of carbonaceous waste & coal

Waste processing for chemical recycling

Closed Carbon Cycle!

“Green” H₂ from renewable electricity

Chemical products from domestic carbon resources

Gasification of carbonaceous waste & coal

Waste processing for chemical recycling

Syngas processing & chemicals synthesis

Minimized CO₂ emissions

Thermochemical conversion processes:

- Pyrolysis
- Gasification

Feedstock

Char

Volatile
High pressure drop-tube pyrolysis – Feedstock

Feedstock characterization

**Feedstock** ➔ Lignite (Central German coal-mining district)

- **Drying (105 °C)**
- **Sieving**
- **Pyrolysis in PYMEQ**
- **Condensate (+THF)**
- **Analysis**
- **Destillation**
- **THF + Water**
- **Analysis**
- **Char**
- **Gas**
- **Analysis**
- **MS, GC**

**Particle size distribution of 63…200 µm**

- $x_{10} = 72$ µm
- $x_{50} = 131$ µm
- $x_{90} = 190$ µm
- $d_v = 131$ µm
- $\phi = 0.89$

**Process balancing, reaction kinetics, residence time, ...**

**Process modellling, process simulation and process optimization**
High pressure drop-tube pyrolysis – Drop-tube reactor

High pressure drop-tube reactor PYMEQ

- **PY**rolysis
- **M**easurement
- **E**quipment

**Feeding system**
- Max. 1.0 l, ≤ 10 g/min
- 40…1,000 μm
- Moisture ≤ 10 wt.%

**Process conditions**
- T ≤ 800 °C
- p ≤ 100 bar (g)
- Ar, H₂, CO₂, CH₄, steam and mixtures

**Equipment**
- Heated length: 2.5 m
- Reactor ID: 20 mm
- 2-stage condensing system (-20 °C)
- Online MS
- 1 optical port
High pressure drop-tube pyrolysis – Characterization methods

Process balancing at high pressure drop-tube reactor PYMEQ

**Ultimate analysis**

<table>
<thead>
<tr>
<th>Element</th>
<th>Coal wt.-%</th>
<th>Char wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>62.6</td>
<td>72.9</td>
</tr>
<tr>
<td>H</td>
<td>4.7</td>
<td>1.8</td>
</tr>
<tr>
<td>N</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>S_C</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>O</td>
<td>17.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**Proximate analysis, wt.-%**

<table>
<thead>
<tr>
<th>Component</th>
<th>Coal wt.-%</th>
<th>Char wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water*</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>Ash (dry, 815 °C)</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>Volatiles (dry)</td>
<td>50.9</td>
<td></td>
</tr>
<tr>
<td>C_{fix} (dry)</td>
<td>35.4</td>
<td></td>
</tr>
</tbody>
</table>

**Energy content, kJ/kg**

<table>
<thead>
<tr>
<th>Condition</th>
<th>HHV (dry)</th>
<th>LHV (dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25,350</td>
<td>24,329</td>
</tr>
</tbody>
</table>

**Pyrolysis gas**

<table>
<thead>
<tr>
<th>Component</th>
<th>Vol.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2</td>
<td>30.1</td>
</tr>
<tr>
<td>CO</td>
<td>18.2</td>
</tr>
<tr>
<td>CO_2</td>
<td>21.0</td>
</tr>
<tr>
<td>CH_4</td>
<td>28.0</td>
</tr>
<tr>
<td>H_2S</td>
<td>2.1</td>
</tr>
<tr>
<td>C_{2+}</td>
<td>0.6</td>
</tr>
<tr>
<td>LHV</td>
<td>16.5 MJ/m³</td>
</tr>
</tbody>
</table>

**Experimental matrix**

<table>
<thead>
<tr>
<th>Condition</th>
<th>600 °C</th>
<th>700 °C</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 bar</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>10 bar</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>20 bar</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>40 bar</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>80 bar</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>100 bar</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

**Char**

H 11.2 wt.-%
O 88.8 wt.-%

**Coal**

C 62.6 wt.-%
H 4.7 wt.-%
N 0.6 wt.-%
S_C 1.2 wt.-%
O 17.2 wt.-%

**Char**

C 72.9 wt.-%
H 1.8 wt.-%
N 0.6 wt.-%
S_C 0.7 wt.-%
O 0.7 wt.-%

**Pyrolysis gas**

H 11.2 wt.-%
O 88.8 wt.-%

**Experimental matrix**

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<tr>
<td>20 bar</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>40 bar</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>80 bar</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>100 bar</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>
High pressure drop-tube pyrolysis – Results of pyrolysis investigations

Product yields (heated reactor length = 2.5 m)

- **20 barg**
  - Temperature in °C: 600, 700, 800
  - Yield Tar/Oil:
    - 600°C: 10.7
    - 700°C: 9.3
    - 800°C: 5.3
  - Product yields in wt.-%:
    - 600°C: 60.3
    - 700°C: 55.9
    - 800°C: 51.2

- **800 °C**
  - Pressure in barg: 5, 10, 20, 40, 80, 100
  - Product yields in wt.-%:
    - 5 barg: 54.9
    - 10 barg: 58.0
    - 20 barg: 51.2
    - 40 barg: 51.0
    - 80 barg: 55.5
    - 100 barg: 52.9

- **T ↑ → char ↓**
- **gas ↑**
- **condensate ↓**
- Significant degradation of tar/oil fraction at higher temperatures

- No consistent influence of process pressure
- Maximum of char yield and condensate yield at 10 barg
High pressure drop-tube pyrolysis – Reaction kinetics (model)

**Model for determination of kinetic parameters**

- Representation of pyrolysis process as decomposition reaction

\[
\text{Coal} \rightarrow \text{Char} + \text{Volatiles}
\]

- Condensable components (reaction water, tar/oil fraction)
- Pyrolysis gas (CH₄, CO, CO₂, H₂, C₂H₆, C₂H₄, C₂H₂, C₃H₈, C₃H₆, C₃H₄, …)

- Mathematical expression:

\[
- \frac{dX_i}{dt} = k(T) \cdot X_i^n \quad \text{with} \quad X_i = b(V_{i,\text{max}} - V_i)
\]

\[
\frac{dV_i}{dt} = k(V_{i,\text{max}} - V_i)^n \quad \text{with} \quad V_i(t = 0) = 0
\]

\(X_i = \) concentration of reactive groups in the coal macro molecule
High pressure drop-tube pyrolysis – Reaction kinetics (model)

Model for determination of kinetic parameters

- Description of pyrolysis process by isothermal approach of independent parallel reactions
- Substitution of $k(T)$ by Arrhenius equation

$$
\text{for } n = 1 \rightarrow \ln \left[ \ln \left( \frac{V_{max}}{t} \right) \right] = \ln(k_\infty) \frac{E_A}{R} \cdot \frac{1}{T}
$$

$$
\text{for } n = 2 \rightarrow \ln \left[ \frac{V}{V_{max} \cdot (V_{max} - V) \cdot t} \right] = \ln(k_\infty) \frac{E_A}{R} \cdot \frac{1}{T}
$$

- Recalculation/Modelling of gas formation:

$$
\text{for } n = 1 \rightarrow V = V_{max} \cdot \left( 1 - \exp^{-k(T) \cdot t} \right)
$$

$$
\text{for } n = 2 \rightarrow V = \frac{V_{max}^2}{V_{max} + \frac{1}{k(T) \cdot t}}
$$

Arrhenius plot
### Kinetic parameters of main gas components

<table>
<thead>
<tr>
<th></th>
<th>20 barg</th>
<th>40 barg</th>
<th>80 barg</th>
<th>20 barg</th>
<th>40 barg</th>
<th>80 barg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_A$ in kJ/mol</td>
<td>$k_0$ in s$^{-1}$</td>
<td>$E_A$ in kJ/mol</td>
<td>$k_0$ in s$^{-1}$</td>
<td>$E_A$ in kJ/mol</td>
<td>$k_0$ in s$^{-1}$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>126</td>
<td>354,978</td>
<td>103</td>
<td>3,690</td>
<td>140</td>
<td>1.4E+06</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>73</td>
<td>599</td>
<td>89</td>
<td>1,321</td>
<td>61</td>
<td>69</td>
</tr>
<tr>
<td>CO</td>
<td>100</td>
<td>7,413</td>
<td>137</td>
<td>2.4E+05</td>
<td>158</td>
<td>1.1E+07</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>27</td>
<td>5</td>
<td>60</td>
<td>57</td>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td>Total Gas</td>
<td>65</td>
<td>254</td>
<td>80</td>
<td>392</td>
<td>52</td>
<td>34</td>
</tr>
</tbody>
</table>

- General tendency to higher values for higher overall pressures (except CH$_4$)
- Gas formation is inhibited by high pressure
- $E_A$: CO$_2$ < CH$_4$ < CO < H$_2$ (valid for n = 1 and n = 2)
Formation of hydrogen and methane

**Hydrogen formation**
- Product of at least one independent reaction → curve fitting $n = 1$

**Methane formation**
- Product of at least two independent reactions → curve fitting $n = 2$
Formation of carbon monoxide and carbon dioxide

Carbon monoxide formation
- Product of at least two independent reactions → curve fitting $n = 2$

Carbon dioxide formation
- Product of at least two independent reactions → curve fitting $n = 2$
High pressure drop-tube pyrolysis

Summary and outlook

- Strong influence of temperature but less influence of total pressure on product yields
- Determined kinetic parameters comparable to literature
- Formation of main pyrolysis gas components can be described (in terms of residence time) by approach of independent parallel reactions

Future Plans:
- Further appropriate pyrolysis models for kinetics
- Additional feedstocks (waste materials), also as blends with lignite
- Determination of char reactivity by TG-measurements using modified magnetic suspension balance with forced flow through sample containers

Exemplary experimental matrix PYMEQ

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_1$ (5 bar)</td>
<td>x x x x x</td>
</tr>
<tr>
<td>$p_2$ (10 bar)</td>
<td>x</td>
</tr>
<tr>
<td>$p_3$ (20 bar)</td>
<td>x x x x x</td>
</tr>
<tr>
<td>$p_4$ (40 bar)</td>
<td>x</td>
</tr>
<tr>
<td>$p_5$ (80 bar)</td>
<td>x x x x x</td>
</tr>
<tr>
<td>$p_6$ (100 bar)</td>
<td>x</td>
</tr>
</tbody>
</table>
Thanks for your attention!

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