The overall reaction kinetics for the devolatilization of large coal particles

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Background & Motivation

The combustion and gasification of coal consists of a short pyrolysis period followed by a long combustion or gasification period the duration which depends on the coal properties, type of reactor and operating conditions.

Thus, since current processes needs to be improved and new processes developed using different coals it is essential that that more research be devoted to detailed analyses of both periods especially with respect to reaction kinetics which determines the reaction times.

The pyrolysis period involving the evolution of volatiles (composition and rate) and physical structural changes affects the reactions in the surrounding gas phase and within the particles (char-gas reactions). This has been identified and considered to be important for the operation of the overall conversion process. Low–ash, low-rank coals are favourable for efficient operation of combustors.
Background & Motivation

The modeling of the pyrolysis is very complex and can consist of a combination of the following reaction/transport mechanisms:

1. Chemical kinetics for the fraction loss of volatiles,
2. Heat transfer within the particle,
3. Mass transfer of volatiles in the porous structure.

The particle size and volume change of the coal particles also needs to be considered which together with the temperature will determine the importance of the different reaction/transport mechanisms.

The overall kinetics for pulverised coal at moderate temperatures can be controlled by the chemical kinetic model only (isothermal) whereas for medium size and very large particles all the mechanisms mentioned above may be important.
Background & Motivation

From an industrial perspective the application would be

(1) pulverized combustion/gasification using fine particles which requires coal preparation and fine coal handling.
(2) fluidized bed combustion requiring medium size particles (1mm to 3mm diameter), and
(3) moving bed gasification for which large particles from 25 to 50 mm (diameter) are used.
Objectives and Scope

The overall objective of the investigation was to determine the properties of the volatiles produced and the validation of an integrated reaction rate model for the devolatilization of large coal particles. The aim is to contribute to the modeling of moving bed gasifiers using typical South African coals.

Scope

In order to achieve the abovementioned objectives the following was performed:

1. Detailed characterization of selected coals.
2. Devolatilization experiments with a specially designed furnace
3. Kinetic studies with thermogravimetric analysers
Coal characterisation

(1) Proximate analysis
(2) Ultimate Analysis
(3) Petrographic Analysis
(4) XRD Analysis
(5) ss NMR Analysis
## Coal characterisation results

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>(A) INY</th>
<th>(B) UMZ</th>
<th>(C) G#5</th>
<th>(D) TSH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air dry</td>
<td>Dry</td>
<td>Air dry</td>
<td>Dry</td>
</tr>
<tr>
<td><strong>PROXIMATE ANALYSIS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inherent moisture %</td>
<td>2.1</td>
<td>0.0</td>
<td>2.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Ash %</td>
<td>18.2</td>
<td>18.6</td>
<td>14.8</td>
<td>15.2</td>
</tr>
<tr>
<td>Volatiles %</td>
<td>25.0</td>
<td>25.5</td>
<td>24.5</td>
<td>25.2</td>
</tr>
<tr>
<td>Fixed Carbon %</td>
<td>54.7</td>
<td>55.9</td>
<td>57.9</td>
<td>59.6</td>
</tr>
<tr>
<td><strong>TOTAL</strong> %</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td><strong>FUEL RATIO (FC/VM)</strong></td>
<td>2.2</td>
<td>2.4</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>GROSS CALORIFIC VALUE</strong></td>
<td>MJ/kg</td>
<td>26.32</td>
<td>26.9</td>
<td>26.91</td>
</tr>
<tr>
<td>GRADE (BASED ON CV, AD BASIS)</td>
<td>Grade C</td>
<td>Grade B</td>
<td>Grade A</td>
<td>Grade Sp</td>
</tr>
<tr>
<td>ATOMIC H/C RATIO</td>
<td>0.69</td>
<td>0.62</td>
<td>0.83</td>
<td>0.66</td>
</tr>
<tr>
<td>ATOMIC O/C RATIO</td>
<td>0.09</td>
<td>0.08</td>
<td>0.11</td>
<td>0.01</td>
</tr>
</tbody>
</table>
# Coal characterisation results

<table>
<thead>
<tr>
<th>FREE SWELLING INDEX</th>
<th>(A) INY</th>
<th>(B) UMZ</th>
<th>(C) G#5</th>
<th>(D) TSH</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.m.b</td>
<td>m.m.f</td>
<td>m.m.b</td>
<td>m.m.f</td>
<td>m.m.b</td>
</tr>
<tr>
<td>Air dry</td>
<td>Dry basis</td>
<td>Air dry</td>
<td>Dry basis</td>
<td>Air dry</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
<td>9.0</td>
<td></td>
</tr>
</tbody>
</table>

**COAL TYPE BASED ON FSI**
- Weakly caking
- Non caking
- Non caking
- Strongly caking

**FISCHER TAR ANALYSES**

| | (A) INY | (B) UMZ | (C) G#5 | (D) TSH |
| | m.m.b | m.m.f | m.m.b | m.m.f | m.m.b | m.m.f |
| Coke | % | 82.98 | 83.63 | 72.84 | 85.56 |
| Tar | % | 6.69 | 5.80 | 11.29 | 7.62 |
| Gas | % | 4.69 | 4.17 | 5.97 | 5.27 |
| Water | % | 5.65 | 6.4 | 9.9 | 1.55 |
| TOTAL | % | 100.01 | 100.00 | 100.00 | 100.00 |

## MACERAL ANALYSIS

<table>
<thead>
<tr>
<th>Total</th>
<th>(A) INY</th>
<th>(B) UMZ</th>
<th>(C) G#5</th>
<th>(D) TSH</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.m.b</td>
<td>m.m.f</td>
<td>m.m.b</td>
<td>m.m.f</td>
<td>m.m.b</td>
</tr>
<tr>
<td>Total Vitrinite</td>
<td>vol.%</td>
<td>33.0</td>
<td>36.7</td>
<td>22.0</td>
</tr>
<tr>
<td>Total Liptinite</td>
<td>vol.%</td>
<td>3.0</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td>Total Inertinite</td>
<td>vol.%</td>
<td>54.0</td>
<td>60.0</td>
<td>65.0</td>
</tr>
<tr>
<td>Visible Minerals</td>
<td>vol.%</td>
<td>10.0</td>
<td>-</td>
<td>10.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>vol.%</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Coal characterisation results

**XRD (Demin. Coal): Calculating fraction of Amorphous Carbon**

<table>
<thead>
<tr>
<th>XRD PARAMETERS</th>
<th>(A) INY</th>
<th>(B) UMZ</th>
<th>(C)G#5</th>
<th>(D) TSH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction of amorphous carbon</td>
<td>$X_a$</td>
<td>0.58</td>
<td>0.59</td>
<td>0.67</td>
</tr>
<tr>
<td>Aromaticity</td>
<td>$f_a$</td>
<td>0.80</td>
<td>0.79</td>
<td>0.70</td>
</tr>
<tr>
<td>Degree of disorder index</td>
<td>$DOI$</td>
<td>0.68</td>
<td>0.69</td>
<td>0.77</td>
</tr>
</tbody>
</table>
Coal characterisation results

\( ^{13}\text{C} \text{NMR (CP-MAS)} \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cluster size</th>
<th>Crosslinks</th>
</tr>
</thead>
<tbody>
<tr>
<td>INY</td>
<td>21</td>
<td>5.5</td>
</tr>
<tr>
<td>UMZ</td>
<td>19</td>
<td>4.5</td>
</tr>
<tr>
<td>G#5</td>
<td>20</td>
<td>4.6</td>
</tr>
<tr>
<td>TSH</td>
<td>24</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\[ \text{Percentage molar basis} (\%) \]

\[ \text{B.L.} \quad \text{S.C.} \]

(A) INY, (B) UMZ, (C) G#5, (D) TSH
Devolatilization Experiments
Properties of volatiles
Gas and Tar Capturing Apparatus

- Primary tar traps
- Secondary tar traps
- Oven
- Cold gate valve
- Hot gate valve
- Insulative cladding and heating trace
- Outlet
- Reactor
- Thermocouple read-outs
- Cirrus online mass spectrometer
- Data acquisition 1
- Data acquisition 2
- Tap off for GC-sampling
- Off-gas
- N₂ gas bottles
- Valve stem handle
- Distributor flange
- Oven temperature controllers
- Gas distributor
- Reactor bottom flange
- Gas warming coil
- Pressure release purge
- Gas purge

Product capture and analysis
Product generation and capture

Effect of temperature (450°C and 750°C):

Devolatilization of 5 mm particles

Devolatilization of 20 mm particles
Product generation and capture

Effect of particle size (5 mm and 20 mm):

Devolatilization at 450°C

Devolatilization at 750°C
Product generation and capture

Effect of coal type at 450°C (2 inertinite rich coals and 2 vitrinite-rich coals):

\[ MI = (HV)^{2.5} \cdot RF \]
\[ RF = \left[ \frac{LIP + \left( \frac{VIT}{R^2} \right)}{INT^{1.25}} \right] \]
\[ HHV = \frac{HV}{30} \]

Product generation and capture

Gas evolution (Comparison between temperatures for 5mm-Coal B):

<table>
<thead>
<tr>
<th>Devolatilization product</th>
<th>UMZ_450C_5</th>
<th>UMZ_750C_5</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.03</td>
<td>1.45</td>
</tr>
<tr>
<td>CH4</td>
<td>0.66</td>
<td>3.06</td>
</tr>
<tr>
<td>CO</td>
<td>0.29</td>
<td>4.68</td>
</tr>
<tr>
<td>CO2</td>
<td>1.12</td>
<td>3.24</td>
</tr>
<tr>
<td>C2H4</td>
<td>0.07</td>
<td>0.79</td>
</tr>
<tr>
<td>C2H6</td>
<td>0.34</td>
<td>0.43</td>
</tr>
<tr>
<td>C3H6</td>
<td>0.09</td>
<td>0.45</td>
</tr>
<tr>
<td>C3H8</td>
<td>0.14</td>
<td>0.06</td>
</tr>
<tr>
<td>C4's</td>
<td>0.15</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Product generation and capture

Gas evolution (Comparison between particle sizes at 750°C- Coal B):
The integrated reaction model for large particles

1. Intrinsic kinetics (from fine particle kinetics)
2. Conservation of heat
3. Conservation of mass
4. Particle properties
5. Velocity field
Components of integrated model

**Intrinsic kinetics:**

\[ \frac{\partial V_T}{\partial t} = V^* \cdot \frac{3}{R_p^3} \int_0^{R_p} \sum_{i=1}^{n} f_i k_i \exp\left(-\frac{E_{i,a}}{RT}\right) \cdot (1 - \alpha_i) \cdot r^2 \, dr \]

**Conservation of heat:**

\[ \frac{\partial (\rho_s T)}{\partial t} + \frac{c_{p,v}}{c_{p,s}} \cdot \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 u \rho_v T\right) = \frac{\lambda_e}{c_{p,s}} \cdot \frac{1}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) \right) + \frac{1}{c_{p,s}} \cdot R_v \left(-\Delta H\right) - \frac{\rho_s T}{v} \cdot \frac{\partial v}{\partial t} \]
Components of integrated model

Conservation of mass:

$$\frac{\partial(\theta \rho_v)}{\partial t} + \frac{\partial}{\partial r}(u \rho_v) = R_v - \frac{\theta \rho_v}{v} \cdot \frac{\partial v}{\partial t}$$

Rate of volatile transfer
Radial flux of volatiles
Volatile generation
Mass flux restriction due to swelling/shrinkage

Variation of bulk density as result of volume change

$$\frac{\partial \rho_s}{\partial t} = -R_v - \rho_s \frac{\partial v}{v} \frac{\partial t}{\partial t}$$

Darcy’s equation for velocity in terms of pressure

$$u = -\frac{K_p}{\mu_v} \frac{\partial P}{\partial r};$$
Experimentation

**Fine particle**: Determination of intrinsic kinetics.

*High Pressure, High Temperature TGA.*
Typical DTG curve of coal devolatilization.
Experimentation

Large Particle for validation of integrated model

Large particle rate behaviour:
Conversion rates of larger coal particles (20 mm) in LPTGA
Rate measurement of devolatilization

Large Particle TGA.

N₂ gas bottle

Data acquisition 1

Furnace

Ceramic pipe

Quartz sample basket

Aluminium tri-pod

Sliding bars

Thermocouple

Gas inlet

5.376 g

Analytical balance

Steel frame
Large particle rate behaviour
Coal A
Large particle rate behaviour

Large particle TGA runs (INY) (Inertinite-rich coal A):

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Coal</th>
<th>Char</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C</td>
<td>![Coal Image]</td>
<td>![Char Image]</td>
</tr>
<tr>
<td>450°C</td>
<td>![Coal Image]</td>
<td>![Char Image]</td>
</tr>
<tr>
<td>550°C</td>
<td>![Coal Image]</td>
<td>![Char Image]</td>
</tr>
<tr>
<td>600°C</td>
<td>![Coal Image]</td>
<td>![Char Image]</td>
</tr>
<tr>
<td>650°C</td>
<td>![Coal Image]</td>
<td>![Char Image]</td>
</tr>
<tr>
<td>750°C</td>
<td>![Coal Image]</td>
<td>![Char Image]</td>
</tr>
<tr>
<td>900°C</td>
<td>![Coal Image]</td>
<td>![Char Image]</td>
</tr>
</tbody>
</table>
Large particle rate behaviour

Large particle TGA runs (TSH) (Vitrinite-rich coal- D):

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Images</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>450°C</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>550°C</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>600°C</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>650°C</td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>750°C</td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>900°C</td>
<td><img src="image7.png" alt="Image" /></td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Evaluation of integrated reaction model (Coal A)

1. Intrinsic kinetics
2. Conservation of heat
3. Conservation of mass
Reaction Rate Modelling

Lumped overall reaction
Deconvolution - Gaussian curves

\[
\frac{dX}{dt} = f_a k_a (1 - X_a) + f_b k_b (1 - X_b) + f_g k_g (1 - X_g) + \sum_{i=1}^{3} f_i k_i (1 - X_i)
\]

with \( f_i = \text{fractions} \)

Integration and each fraction evaluated
Coates-Redfern for kinetic parameters
Modelling CoaLA

Intrinsic kinetics (INY, 25K/min):

<table>
<thead>
<tr>
<th>No.</th>
<th>$f_i$</th>
<th>$k_{0,i} (\text{min}^{-1})$</th>
<th>$E_i (\text{kJ/mol})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM</td>
<td>0.09</td>
<td>$3.02 \times 10^5$</td>
<td>40.6</td>
</tr>
<tr>
<td>MP</td>
<td>$3.51 \times 10^{-3}$</td>
<td>$1.89 \times 10^7$</td>
<td>68.5</td>
</tr>
<tr>
<td>PP</td>
<td>0.26</td>
<td>$1.01 \times 10^{11}$</td>
<td>160.4</td>
</tr>
<tr>
<td>SPI</td>
<td>0.54</td>
<td>$2.14 \times 10^2$</td>
<td>49.7</td>
</tr>
<tr>
<td>SPIII</td>
<td>0.10</td>
<td>$1.89 \times 10^{13}$</td>
<td>276.1</td>
</tr>
</tbody>
</table>
Heat transfer Modelling

Benchmarking the heat transfer model [22]:

Governing equations:
\[
\frac{\partial T}{\partial t} = \frac{k}{\rho c_p} \cdot \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right)
\]

\[k \frac{\partial T}{\partial r} = h(T_\infty - T_s) + \varepsilon \sigma \left( T_{surr}^4 - T_s^4 \right); \quad r = R\]

\[\frac{\partial T}{\partial r} = 0; \quad r = 0\]

\[T_0 = 293.15 \, K; \quad t = 0\]

\[T_{s,0} = 293.15 \, K; \quad r = R\]

Constants:

\[\tilde{k} = 0.26 \, W / m.K\]

\[\tilde{c}_p = 1180 \, J / kg.K\]

\[\tilde{h} = 12.89 \, W / m^2.K\]

\[\sigma = 5.67 \times 10^{-8} \, W / m^2.K^4\]

\[R = 0.02 \, m\]

\[\tilde{\rho} = 1500 \, kg / m^3\]

\[\varepsilon = 0.85\]

\[Nu = 2 + 0.6 \text{Re}^{0.5} \text{Pr}^{0.333}\]
**Integrated Model**

Combined kinetics, mass and heat transfer (20 mm INY particles, 1073 K):

- $T_{\text{ext}} = 1173$ K
- $T_{\text{ext}} = 1023$ K
- $T_{\text{ext}} = 923$ K
- $T_{\text{ext}} = 823$ K
- $T_{\text{ext}} = 723$ K
- $T_{\text{ext}} = 623$ K
Conclusions

Four typical South African coals were examined consisting of vitrinite-, inertinite- and liptinite rich macerals respectively and with aromaticities varying between 0.67 and 0.81 (XRD and NMR) which are considered as important determining parameters for volatile evolution and rate of devolatization production.

The evolution volatiles consisting of gases and tars from large coal particles 5mm and 20mm respectively and at two different temperatures different temperatures 450 and 750 deg C were examined successfully with experimentation with a specially constructed reactor. This vertical reactor consisted of dropping coal particles into a heat chamber from which the volatiles are generated followed by on-line measurement of the gasses and collection of the tars.

The important results obtained from the devolatilization experimentation were that the compositions of the tars were accurately measured with GC-MS, NMR and XRD which revealed properties dependant on the parent coal properties and very useful for further processing.
Conclusions

The reaction kinetics for the devolatilization involving the production of the gases and tars only was determined with a thermogravimetric analysis using fine coal particles and a reaction rate model involving analyzing different fractions consisting of moisture, primary and secondary products characteristic of coal devolatilization.

An integrated non-isothermal model consisting of chemical reaction kinetics, heat and mass transfer with structural changes for large particles (5 and 20 mm) was successfully evaluated with results obtained from a specially designed large particle thermogravimetric analyser.