Soot Formation during Pyrolysis and Gasification of Asphaltene

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Contents

- Introduction
- Soot formation
- Experiments
- Results & Discussion
- Summary
Canada’s Oilsands

- 97% of Canada’s oil reserves are in oil sands
- Canada’s raw bitumen production by 2030: 5.33 mbpd
- Athabasca oil sands contain 8 to 14% bitumen

About Canada’s oil sands, Canadian Association of Petroleum Producers (CAPP), 2012.
Canada’s Oilsands

Oil Sands Composition (Wt%)

- Mineral Solids: 83-88%
- Bitumen: 8-14%
- Water: 3-5%

Recovered Bitumen
Bitumen Recovery

- 20% of deposits are close to surface
- 80% of the deposits are at greater depths


9/6/2015
Bitumen Upgrading

Kerr et al, The long lake project-First field integration of SAGD and upgrading, International Thermal Operations and heavy oil symposium, Canada, Nov 2002
Asphaltene in Athabascan Oilsands

![Molecular structure of asphaltene]

- Heaviest and most polar molecular with H: C ratio is approximately 1: 1.10 to 1.20
- Insoluble in alkanes (C5, n-C7) and soluble in aromatics
- Most V, Ni and S are concentrated in asphaltenes

**Ultimate Analysis**

- Carbon: 82.68%
- Hydrogen: 8.34%
- Sulfur: 7.75%
- Nitrogen: 1.2%
- Oxygen: 0.03%

**Proximate Analysis**

- Volatiles: 63%
- Fixed carbon: 36.3%
- Ash: 0.6%
- Moisture: 0.1%


Soot Formation during Pyrolysis

Soot Formation

- The term Soot is given to the sub-micron particles formed during combustion under sub-stoichiometric conditions.

- Soot usually forms at 1000 to 2500 °C.

- Trace metals like V & Ni in asphaltene cause erosion.

- If soot encapsulate the metals, the erosion can be avoided.

Stanmore, B. R. et al., Carbon, 2001, 39, 2247 –2268
Objectives

To investigate the effect of operating parameters on the character of soot formed during the pyrolysis of asphaltene in an electrically heated Drop Tube Furnace.

<table>
<thead>
<tr>
<th>Process Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed particle size</td>
<td>53-106 µm</td>
</tr>
<tr>
<td></td>
<td>106-150 µm</td>
</tr>
<tr>
<td></td>
<td>150-212 µm</td>
</tr>
<tr>
<td>Temperature</td>
<td>800°C</td>
</tr>
<tr>
<td></td>
<td>1000°C</td>
</tr>
<tr>
<td></td>
<td>1200°C</td>
</tr>
<tr>
<td></td>
<td>1400°C</td>
</tr>
<tr>
<td>Residence Time</td>
<td>5 s</td>
</tr>
<tr>
<td></td>
<td>6.6 s</td>
</tr>
<tr>
<td></td>
<td>8.5 s</td>
</tr>
<tr>
<td></td>
<td>12 s</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
</tr>
</tbody>
</table>
Experimental Set up

**Drop tube furnace**
Mullite / Alumina tube
2.5 in. ID × 5 ft. L
Max Temperature: 1500°C
Atmospheric pressure

Collection of soot on substrate aluminium foil
Effect of feed particle size

Asphaltene feed particle size has no major impact on the soot formed during pyrolysis.
Particle size distribution of soot

The difference in particle size distribution is due to the contamination of soot with large char particles.

Particle size distribution of soot is similar for different feed particle sizes.
Soot collected on different stages looked similar in shape and structure despite the carry over of large char particles to the top stages of cascade impactor.
Soot Formation at 800° C

Mixture of Tar and soot collected on cascade impactor

Dried soot separated from tar
Effect of Temperatures

Average soot particle size decreases with temperature
At higher temperatures, no tar was observed
Effect of Temperatures-Mechanism

At temperatures 727-1027°C, the Tar cracking to form secondary light gases is predominant.

High concentrations of light gases cause surface growth on soot particles formed from primary gas and by tar polymerization.

At higher temperatures (1200-1400°C) the tar cracking reaction is minor compared to primary soot formation from tar.

The decrease in concentration of light gases around
  ➔ lower surface growth reactions and
  ➔ soot particle size is lower

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Soot yield increases with pyrolysis temperature
Effect of Residence time

More residence time $\Rightarrow$ more surface growth
Sulfur & Hydrogen content in Soot

- S & H content in soot decreases with temperature
- S & H content in soot is not affected by residence time.

![Graph showing the decrease of Sulfur and Hydrogen content with temperature and residence time.](image)
Soot on Char, 1000°C

Soot observed on top surface of the char particles
At 1000°C & 1200°C, soot contains more V, Ni, Fe Al, Mg, Ca etc. compared to char, but at 1400°C char contains more.
Conclusions

- **Soot yield**
  - Higher temperature $\Rightarrow$ more yield

- **Soot particle Size**
  - Asphaltene feed size has no significant impact on soot particle size
  - Lower temperatures $\Rightarrow$ higher tar cracking $\Rightarrow$ surface growth
  - Increase in residence time increases surface growth

- **S & H content of soot**
  - Lower temperature $\Rightarrow$ release of aliphatic S $\Rightarrow$ S and H content decreases
  - Residence time has no significant effect
Conclusions contd.

- **Effect on trace elements**
  - At 1000°C and 1200°C soot contains more trace metals like V, Ni, Fe, Al, Mg, Ca etc. compared to char.
  - At 1400°C char contains more trace metals than soot.
Acknowledgements
Thank You!