Effect of heating rate and temperature on pyrolysis of asphaltenes:
A study of char characteristics

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Outline

**Introduction**
- Bigger Picture on Oil sands & Bitumen
- What are Asphaltenes?
- Asphaltenes Gasification
- Importance of char
- Objective

**Experimental**
- Char Preparation
- Characterization

**Results & Discussions**
- Char morphology & composition
- Reactivity

**Conclusions**
Introduction
Oil Sands in Canada

Canada

Oil sands are primarily obtained in Alberta (Western Canada)

3rd Largest Oil Reserves

5th Largest Crude Oil producer

1.8 MMbd

2012

5.21 MMbd

2030

Crude Oil production from Oil sands

Oil Sands in Canada

Oil Sands in Canada
Bitumen
(from Oil sands)

- HEAVY
- Higher Density, Viscosity, S, N, O, Minerals & Carbon Residue (MCR/CCR)
- 15 wt.% Asphaltenes

Oil Sands → Extraction → Bitumen → Upgrading → Crude Oil → Asphaltenes
Asphaltenes

Powdered asphaltenes

- Heaviest fraction of Bitumen/ petroleum liquids \(^8,9,10\)
- 50% of Carbon Residue in Bitumen \(^11,12\)
- Highest Sulfur & Mineral Content
- Complex Structure

- Cause problems during
  - Production
  - Refining
  - Transportation

Archipelago structure
MW: 4133 g/mol \(^13\)
Asphaltenes have no use and pose disposal problems but are high in calorific value.

Gasification can provide a cleaner alternative \(^{14,15,16}\).

Asphaltenes as liquid streams are easier and cost effective to handle than solid coke. \(^{16}\)
Char is important

Gasification

Pyrolysis

Heterogeneous Char gas reactions

Gas phase reactions

Slowest Step $\rightarrow$ Overall Rate of Reaction

- Water gas reaction
- Boudouard Reaction
- Hydrogenation reaction
Char is important

Gasification

Pyrolysis

Heterogeneous Char gas reactions

Gas phase reactions

Amount and characteristics of char and volatiles$^{17-22}$

- Temperature
- Residence Time
- Heating Rate
- Feed Size
Objective

Char
- Structure & Composition
- Morphology
- Global Reactivity

Operating Temperature

Residence time at temperature

Heating rate
Char Preparation

- 150-212 um solid asphaltene feed
- Mullite /Alumina tube
- 65 mm ID X 153 cm height
- Electrical heating
- Atmospheric pressure
- Air and water cooled feeder probe
- \( \text{N}_2 \) (entraining gas)
Characterization

- Proximate & Elemental Analysis
- Scanning Electron Microscope (SEM) & Energy Dispersive X-Ray (EDX)
- X-Ray Diffraction (XRD)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- Thermogravimetry (TGA)
Results & Discussions
## Operational Parameters

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Nominal Temperature of DTF (°C)</th>
<th>Nominal Residence Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C Char</td>
<td>800</td>
<td>8.4</td>
</tr>
<tr>
<td>1000 °C Char</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>1200 °C Char</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>1400 °C Char</td>
<td>1400</td>
<td></td>
</tr>
<tr>
<td>11.8 s Char</td>
<td>1200</td>
<td>11.8</td>
</tr>
<tr>
<td>8.4 s Char</td>
<td></td>
<td>8.4</td>
</tr>
<tr>
<td>6.5 s Char</td>
<td></td>
<td>6.5</td>
</tr>
<tr>
<td>4.9s Char</td>
<td></td>
<td>4.9</td>
</tr>
</tbody>
</table>

**Pressure:** 1 atm  
**Feed Size:** 150-212 µm
Volatile & Fixed Carbon

Temperature \( \uparrow \) Residence Time \( \Rightarrow \) Volatiles \( \downarrow \) FC \( \uparrow \)

Temperature more pronounced effect
H/C, Sulfur & Carbon

- Temperature \( \uparrow \) Residence Time \( \Rightarrow \) H/C \( \downarrow \) S \( \downarrow \) C \( \uparrow \)
- N, O content also decreases
- Rate of decrease of H/C and S Decreases at higher temperatures
Maximum weight loss region occurs between **350-500 °C** with a maxima at **450°C**

- **Asphaltenes**
- **Char**

**Incomplete pyrolysis**

**Re-condensed volatiles (minor)**
Infrared Spectra

- CH -, aromatic CH
- CH₂- and CH- (wag)
- -OH carboxylic acid
- C=O carbonyl
- CH₂-S (wag)

Wave Number (cm⁻¹)
Infrared Spectra

- CH\(-\), aromatic CH
- CH\(_2\)- and CH\(-\) (wag)

Wave Number (cm\(^{-1}\))

4.9 s Char
6.5 s Char
11.8 s Char
1400 °C Char
1200 °C Char/ 8.4s char
1000 °C Char
800 °C Char
Asphaltenes
X-Ray Diffraction

Crystalline reflection \((00l)\) (turbostratic carbon)

Turbostratic Carbon / Graphitization\(^{24}\)↑
Temperature ↑
Residence time change not much effect
Analysis of trace metals

- V, Ni most abundant in petroleum \(^{25,26}\) (porphyrinic and non-porphyrinic)
- V, Ni accumulates in char
Discussions so far

- **Ash, V, Ni accumulates** in char (0.60 wt.% asphaltenes and 2.18 wt.% ash 1400 °C Char)

- **Initially** H/C ratio decreases fast due to de-alkylation and removal of H$_2$S. At Higher Temperatures decrease is slow due to condensation & peri-condensation$^{27}$ (and graphitization)

- High Heating Rates → **Lower Char Yield**

- **Thiophenic Sulfur remains** while **aliphatic Sulfur** is lost as H$_2$S. (IR Spectra and Elemental Analysis support). Lost early as C-S < C-C$^{28}$

  (Asphaltenes 40% aliphatic S; and 60% thiophenic S$^{23}$)
Morphological Study (SEM)

Temperature

Nominal Particle Size

Bulk Density

Fraction of fragmented particles

Residence Time ➔ No noticeable change in morphology

*Similar magnifications 500X
SEM of Char

1200 °C Char Cross-section

1000X BSE SEM

Soot on Char Surface

25000X SE SEM

- Structure of Char hollow “Cenosphere” with a vesicular porous wall
- White dots are minute soot deposits on char surface
EDX Mapping of Char

- V & Ni in minute quantities
- Aluminosilicates and iron oxides discrete particles
- Sulfur evenly (more in bigger sized)

EDX Mapping of 1200 °C Char (300X magnification)
SEM of Low Heating Rate Char

Macro-porosity increases at higher temperatures

*Similar magnifications 500X
Discussion on Char Morphology

- Nominal particle size decreases and fragmentation increases at higher temperatures, thicker walls.

- Smooth surface of char could signify initial rapid melting of asphaltenes.

- Observable Porosity ↑ Higher Temperatures

- Residence time (5-12s) less pronounced effect
Char Steam (20%) Reactivity

Temperature

Residence Time

Temperature $\uparrow$

Residence Time $\uparrow$

global char steam reaction rate $\downarrow$

Less pronounced for Residence Time
Char CO$_2$(100%) Reactivity

Temperature

- 800 °C Char
- 1000 °C Char
- 1200 °C Char
- 1400 °C Char

Residence Time

- 11.8 s Char
- 8.4 s Char
- 6.5 s Char
- 4.9 s Char

Temperature ↑
Residence Time ↑

global char CO$_2$ reaction rate ↓
(Boudouard Reaction)
Discussion on Char global reactivity

- Char obtained at **higher temperature** have a **decreased reactivity** due to **ordering of carbon structure** (graphitization)\(^{30-32}\) or **thermal annealing** process\(^{33}\). May explain increase loss due to increase in residence time as well.

- **800 Deg. Char** significantly **higher reactivity**. Great **difference in morphology**. **Decrease in micro-porosity** of char at higher temperatures and an **increase in** observed **macro-porosity**.\(^{34}\)
Conclusion
Pyrolysis temperature, residence time at temperature & heating rate affect the morphology, structure and reactivity of chars.

- Increase in operating temperature
  - Global gasification reactivity
  - Nominal particle size
  - H/C Ratio, Number of functional groups, N, S, O, Volatile matter
  - Aromaticity
  - Graphitization
  - Macro-porosity

- Increase in residence time at temperature (less pronounced effect)
  - Global gasification reactivity
  - H/C Ratio, Number of functional groups, N, S, O, Volatile matter
  - Change in morphology, aromaticity & graphitization not noticeable

- Very high heating rates overcome mass transfer limitations and better pyrolysis occurs

Future Work: Estimation of surface area and intrinsic char reactivity
Acknowledgments
References

3. Image source: http://www.huffingtonpost.ca/2012/03/14/oil-sands-eu-canada_n_1345597.html (retrieved 05/13/2014)
Thanks

Questions ?