

## Thin film pyrolysis of oil sands asphaltenes for structural analysis

Arash Karimi<sup>a</sup>, Murray R Gray<sup>a,\*</sup>, Kuangnan Qian<sup>b</sup>, William N. Olmstead<sup>b</sup>, Howard Freund<sup>b</sup>

<sup>a</sup> Department of Chemical & Materials Engineering, University of Alberta, Edmonton, AB T6G 2V4

<sup>b</sup> ExxonMobil Research & Engineering, 1545 Route 22 East Annandale, NJ 08801-0998

(\* corresponding author: murray.gray@ualberta.ca)

In this study we present the results of analysis of the products of controlled pyrolysis of asphaltenes, in order to gain insight into the molecular structure of this material. Asphaltenes from Alberta bitumen and other sources were spray coated as thin films (ca. 20  $\mu\text{m}$ ) on plates of an iron-nickel alloy with a Curie point selected at the pyrolysis temperature (500°C), which allowed for rapid induction heating to a fixed temperature. The combination of the preparation of the asphaltene samples as a thin film and induction heating minimizes the over cracking and polymerization of the molecular fragments of the asphaltenes by minimizing the trapping of the cracking products in liquid phase [1] as well as suppressing the gas-phase reactions by quenching of the vapour-phase by a flow of cold carrier gas.

The asphaltene-coated plates were assembled on ceramic holders in 6-plate batches in order to react circa 1 g, and the assembly was inserted into the induction furnace. The N<sub>2</sub> carrier gas purged the reaction products from the reaction chamber, then passed through a liquid nitrogen cold trap where the liquid products (vapour plus aerosol droplets) were collected. The liquid products were recovered by rinsing the reactor and the tubing with dichloromethane. The solvent was then evaporated by leaving the solution in a fume hood overnight. The gases from the reactor were collected in a gas bag for analysis by gas chromatography. The remaining materials on the plates were sonicated in toluene followed by filtration and drying to recover the coke.

In contrast to gas-chromatography based flash pyrolysis experiments, the reactor apparatus in the present work facilitated the pyrolysis of sample quantities sufficient for several analytical methods on each batch. In addition, reasonable mass balances were established. Table 1 illustrates examples of the mass balances.

**Table 1.** Examples of mass balances achieved in this study for various asphaltenes.

	Ath C <sub>5</sub> <sup>a</sup>	Ath C <sub>7</sub> <sup>b</sup>	CL C <sub>7</sub> <sup>c</sup>
Initial asphaltenes, g	1.141	1.201	1.190
Total coke	37%	48%	48%
Total liquids	59%	42%	44%
Gases	1%	1%	1%
Total recovered, g	1.121	1.091	1.101
<b>Recovery %</b>	<b>98.2%</b>	<b>90.8%</b>	<b>92.5%</b>

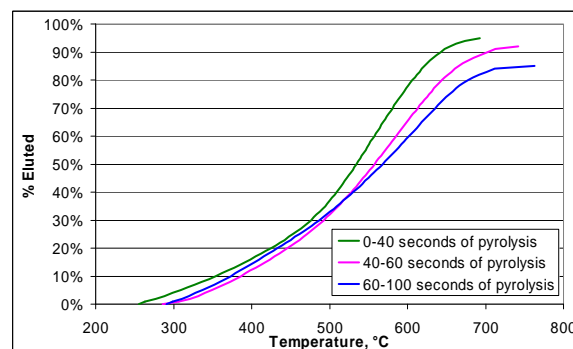
<sup>a</sup> Athabasca nC<sub>5</sub> insolubles

<sup>b</sup> Athabasca nC<sub>7</sub> insolubles

<sup>c</sup> Cold Lake nC<sub>7</sub> insolubles

The n-C<sub>7</sub> insolubles apparently gave more light volatile products than n-C<sub>5</sub> insolubles, which were lost during the evaporation of the solvent used for collecting the liquid products from the reactor. Therefore, the recovery percentage was lower in the former case in all tests. This observation suggests that the molecules with a higher solubility parameter tend to be richer in medium size side chains or bridges (C<sub>5</sub>-C<sub>10</sub>).

The liquid products were analyzed by high temperature simulated distillation (SimDist) according to ASTM D5307. A whole range of molecular fragment sizes corresponding to C<sub>10</sub> to C<sub>100</sub> were detected with this method. The method was unable to detect lighter components (C<sub>5</sub>-C<sub>10</sub>); however these fragments are expected to have mostly evaporated during the solvent removal. The fragments evolved at shorter pyrolysis times tended to be slightly lighter than those released at higher reaction times, but the fragments collected at different reaction times spanned almost the entire detectable boiling range (Fig. 1).



**Fig. 1.** Simulated distillation curves of the liquid products collected after each stage of a three-step consecutive pyrolysis of an Athabasca nC<sub>5</sub> asphaltenes sample.

The next step of this on-going study will be to apply mass spectrometry and <sup>13</sup>C-NMR analysis to these samples and to asphaltenes from other sources.

### References

- [1] Gray, M.R., et al. (2001) Ind. Eng. Chem. Res., 40, 3317-3324.