

## Formation of coke precursors from pyrene-based model compounds

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Understanding coking mechanisms is an important goal for the industry in order to minimize coke yield, increase the liquid yield, and sustain longer operational cycles. The current work investigates the thermal behaviour and coking mechanisms of pyrene-based model compounds.

Tan et al [1] showed that a pyrene-based model compound, with two pyrene groups linked to bipyridine by two ethyl bridges, behaved similarly to asphaltenes in terms of solubility, adsorption, and to some extent association behaviour. Similar structures were used for this study but with a different group in the middle of the molecule, e.g. bipyridine was replaced with a phenyl group (Py-*m*-Phenyl-Py).

This model compound was thermally cracked first in an inert atmosphere in a Thermal Gravimetric analyzer (TGA) to estimate the MicroCarbon Residue (MCR) by ramping the temperature at a constant heating rate to 500°C and keeping it there for 15min. The average solid residue of three runs was 3%. Although the yield of solid residue was low, the coke generated by Py-*m*-Phenyl-Py was produced from liquid phase reactions similar to coking in heavy hydrocarbons. Since the reaction in TGA goes to completion, analyzing this coke gave very little useful information. Microreactor experiments at controlled conversion conditions gave more insight into the cracking products and coking mechanism. The sample was loaded inside a one-end-sealed glass liner inside the microreactor to collect any solid residue that formed, then reacted at 395°C for 15 min in a sand bath. The products were extracted from the reactor by using excess methylene chloride followed by concentration using a rotary evaporator. The conversion of Py-*m*-Phenyl-Py was ~30% and all the products were soluble in methylene chloride which enabled the mass spectrometric analysis of high molecular weight products.

GC-MS was used to analyze the low molecular weight cracked products. The major products observed, shown in figure 1, were pyrene, 1-methylpyrene, parent compound minus methyl-pyrene (m/z 320), parent compound minus pyrene (m/z 334), and the dehydrogenated products of the last two. Most of the other peaks are due to column bleeding which was experienced when high molecular weight compounds were injected. The observed products were consistent with cracking by free-radical mechanisms; the formation of pyrene was observed before [2], and was attributed to radical hydrogen

transfer. Addition products were revealed by MALDI-TOF which showed masses up to m/z 1530 (starting material was 534 g/mol), illustrated in figure 2. All addition products, except a few minor unknowns, were likely generated from the same species: methyl-pyrene, Py-*m*-phenyl-methyl, Py-*m*-phenyl-ethyl, and the parent compound. Adding the weights of these groups gave the masses of the observed addition products. The MALDI peaks showed dehydrogenation of the addition products up to -4H, which may imply cyclization. These coke precursors were likely formed by sequential olefin formation and radical additions in accordance with the proposed mechanism for addition reactions during coking [3].

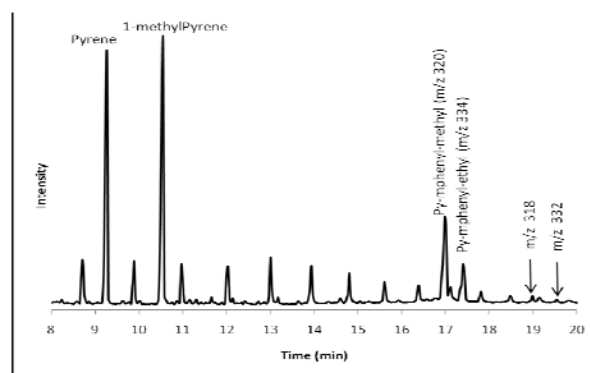


Fig. 1. Major cracked products of Py-*m*Phenyl-Py from GCMS. The unassigned peaks are from column bleeding.

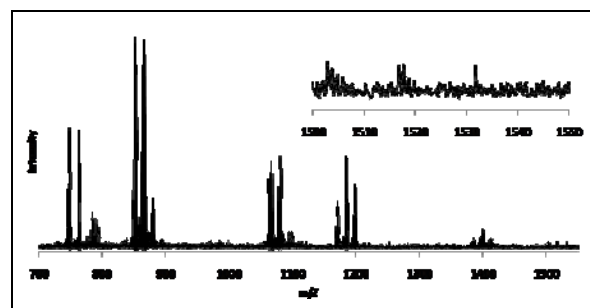


Fig. 2. MALDI-TOF spectra of the addition products. Top region show the peaks formed up to 1530 m/z.

### References

- [1] Tan, X.; Fenniri, H.; and M.R. Gray. Energy & Fuels 2008, 22, 715-720.
- [2] Freund, H. et al. Energy & Fuels 1991, 5, 840-846.
- [3] Gray, M.R. and W. C. McCaffrey. Energy & Fuels 2002, 16, 756-766.