MOLECULAR TRANSFORMATIONS DURING CATALYTIC UPGRADING OF BITUMEN: TOWARDS MONITORING UNDERGROUND REACTORS

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Introduction

Two of the major problems associated with the production of heavy oil and oil sands are low recovery and high environmental impact. In an effort to develop more efficient, environmentally sustainable processes, some in situ upgrading methods are proposed as alternatives to currently used thermal recovery methods. Downhole (or in situ) catalytic upgrading, aiming at some degree of oil refining in the subsurface, is one of these technologies (Greaves and Xia, 2004; Pereira Almão and Larter, 2007; Weissman, 1997).

As opposed to conventional refinery processing, where conditions are strictly controlled, downhole catalytic operations will require to remotely monitoring the conditions achieved, whether the target zones are reached, and the processes taking place in the underground reactor (Weissman, 1997). In this study, we conduct a preliminary investigation of chemical transformations experienced by native reservoir bitumen during catalytic upgrading (and compare them with reactions that take place under non-catalytic upgrading conditions), as potential reaction proxies suitable to be used as monitoring geochemistry tools.

Results

The catalytic upgrading experiment was performed on Athabasca bitumen recovered from core by mechanical extraction. It consisted of a hydrocracking process using an ultra-dispersed (UD) NiWMo nanoscale catalyst (Galarraga, 2011), obtained from water-in-bitumen emulsion of the transition metals. A detailed molecular characterization of the hydrocarbon and polar fractions of the liquid products from bitumen hydrocracking was conducted.

In the saturated hydrocarbon fraction, investigated by gas chromatography – mass spectrometry (GC-MS), changes include the generation of several components, absent in the original bitumen due to its biodegradation level, as well as the removal or dilution of saturated biomarkers. Unexpectedly, adamantane concentrations display almost no apparent variation after 16 hours of hydrocracking at 350°C. This is different from what is observed in non-catalytic hydrous pyrolysis experiments of Athabasca bitumen at the same temperature. In the aromatic hydrocarbon fraction, there is abundant production of mono- and polyaromatic hydrocarbons, and generation of anthracene.

The polar fraction of the feedstock bitumen and the liquid hydrocracking product were investigated by Fourier transform - ion cyclotron resonance -mass spectrometry (FT-ICR-MS; Fig. 1). Observed changes include a decrease in the relative concentration of O2 compound classes (including all DBE groups and carbon numbers) and decrease in relative concentration of S1 and S2 compound classes, although no significant conversion of thiophenic and dibenzothiophenic species is evident (suggesting no sulfur removal from these classes). Pyridinic species appear invariant. Extensive dealkylation and general decrease in number average molecular weight are also observed.

Despite significant desulfurization, no variation in the bitumen bulk sulfur isotopic composition (δ³⁴S) was found.
Conclusions

Thermal cracking appears to be the principal mechanism operating during hydrocracking of Athabasca bitumen, under the investigated conditions. The main identified chemical transformations of the bitumen heavy ends during hydrocracking include dealkylation, increase in aromaticity and decarboxylation. Molecular parameters based on alkylphenanthenes and alkylbenzothiophenes distributions, and the generation of anthracene, show potential as indicators of thermal conversion; they behave similarly to what is observed in hydrous pyrolysis experiments. Some ratios of naphthenes to analogous aromatic compounds (e.g. decalin/naphthalene) are proposed as potential proxies to track hydrogenation reactions (distinctive from pure thermal cracking). They may potentially be used to determine whether catalytic upgrading is operating in the underground by monitoring the produced oil molecular composition during in situ recovery of bitumen; although further investigation is required.

![Full range positive-ion electrospray 12 -T positive-ion FT-ICR mass spectrum of starting Athabasca bitumen feedstock (bottom) and products of hydrocracking at 350 °C and 500 psi H₂ (top). Number average molecular weight (Mn), in Daltons, is shown for each case.](image)

Figure 1

References