



## The Potential of Heavily And Severely Biodegraded Oils to be Partly Upgraded During High Temperature Thermal Recovery Conditions

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### Summary

Upgrading of heavy oil and oil sands under simulated high temperature thermal recovery conditions was conducted to evaluate mechanisms and sources of the produced light hydrocarbon compounds that directly affect oil fluid properties. The main results suggest that the asphaltene fraction is the main source of the light hydrocarbons produced during the upgrading process. Comparing results from oils with different levels of biodegradation, we found that severely biodegraded oils, rich in asphaltene, do have potential for minor upgrading during thermal recovery strategies.

### Introduction

Biodegradation is one of the most dominant post accumulation processes in petroleum reservoirs, responsible for the huge accumulation of heavy and extra-heavy oils in the world. In biodegraded oil reservoirs, biodegradation levels increase with depth towards the oil-water contact. Different gradients have been explained by proximity to the water leg, height of the water leg and the relation between fresh oil input and biodegradation rate<sup>1</sup>. Biodegradation causes systematic changes in the chemistry of the oil due to the preferential removal of the lighter compounds. Variation in the chemical composition of oils are directly related with fluid property changes and consequently related with the flow of the material through a permeable reservoir rock. The complexity of heavy and extra heavy oil reservoirs causes the recovery of this type of reserves to be low, generally not more than 17%, making necessary the development of new methods to optimize production, with low environmental impact. Currently used technologies of *in situ* recovery, such as SAGD (Steam Assisted Gravity Drainage) or CSS (Cyclic steam stimulation), and subsequent surface upgrading processes cause a huge consumption of energy and large greenhouse gas emissions. *In situ* upgrading is being proposed in order to decrease these effects and increase benefits. This process relies on the addition of hydrogen and removal of heteroatoms from crude oils under high temperature conditions in the reservoir, to reduce viscosity and increase the distillable fraction. A detailed knowledge of the upgrading reactions and mechanisms and a better understanding of the chemistry of the products are indispensable for the optimization of upgrading strategies. In this work we evaluate the chemical mechanisms of oil transformation under simulated high temperature thermal recovery conditions and the potential of oils with different levels of biodegradation to generate light compounds that directly affect oil fluid properties.

## Method

Heavy oil and oil sands core samples were pyrolyzed under hydrous and non-hydrous conditions up to 350°C for time periods of up to three days using regular water. Pyrolysates were analyzed for bulk and molecular composition. For molecular investigation, the hydrocarbons and non-hydrocarbons fractions from bitumen and heavy oil were isolated using solid phase extraction methods SPE<sup>2</sup> and GCMS analysis were performed on an Agilent 6890 N network gas chromatograph (GC) system, coupled to an Agilent 5975 XL MSD. The saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes (SARA) content were determined by Thin Layer Chromatography, using an Iatroscan Mk 6S instrument equipped with a flame ionization detector.

## Results

The main results demonstrate that oil sands bitumens are characterized by a lack of n-alkane and isoprenoid alkane hydrocarbons and generate a relatively uniform pattern of n-alkanes up to C30 and isoprenoids such as pristane and phytane, under simulated thermal recovery conditions. SARA content (estimated chromatographically) shows that the production of saturated and aromatic hydrocarbons can be higher from more degraded oil sands. This is more evident in the case of the aromatics (Fig. 1), which content increases by 15% in the oil sand, while in the heavy oil, on the contrary, a slightly decrease in percentage is observed after a 3-day hydrous pyrolysis experiments. The asphaltene fraction decreases, but resins do not show such large variations. Furthermore, when hydrous pyrolysis products of two oil sands with different biodegradation levels are compared, the more biodegraded and originally asphaltene-richer sample (10% more asphaltene content), generates higher concentration of n-alkanes (Fig. 2). These results suggest that the asphaltene fraction is probably the main source of the newly formed saturated and aromatic hydrocarbons, which is consistent with the idea of asphaltene structures rich in aromatic rings interconnected through aliphatic chains and heteroatomic bonds<sup>3-8</sup>; however, resins proposed to be composed by similar structures, are less clearly involved as sources of light hydrocarbons during the upgrading procedure. The generation of bicyclic and tricyclic condensed aromatic molecules, such as C0-C5 naphthalenes, C0-C2 phenanthrenes, dibenzothiophenes and methyl anthracene, some of which are not originally present in the studied oil sands, suggests asphaltene structures with abundant small ring size aromatic systems and a lower degree of condensation than generally claimed (Fig. 3). This was also pointed out by Ignasiak et al. (1977) in their study of Athabasca asphaltene<sup>7</sup>.

Biomarkers such as monoaromatic and triaromatic steroids are destroyed or diluted under the experimental conditions, while variation in terpane parameters, traditionally used to monitor thermal stress and some recently proposed as proxies for process monitoring<sup>11</sup>, appear to be good indicators of the progress of the thermal conversion. The production of adamantanes and new compounds such as methyl anthracene may potentially be good reaction proxies as well.

## Conclusions

➤ The results of high temperature simulated thermal recovery experiments (at hydrous pyrolysis conditions) suggest that the asphaltene fraction is probably the main source of the newly formed saturated and aromatic hydrocarbons. The principal proposed mechanisms are cracking of side chains from aromatic groups and cracking of aliphatic fragments linked through heteroatoms in cyclic systems present in the asphaltene molecular structure. Based on these mechanisms, the abundance of compounds with aryl-alkyl bonds would probably increase the light-compounds generation potential of severely biodegraded oils.

- The different behavior of the asphaltene and resin fractions under the experimental condition suggests differences in their molecular structures and/or stability.
- The results suggest that severely biodegraded oils, with high content of asphaltenes, may have a high potential to be significantly upgraded through very high temperature CSS steam recovery.

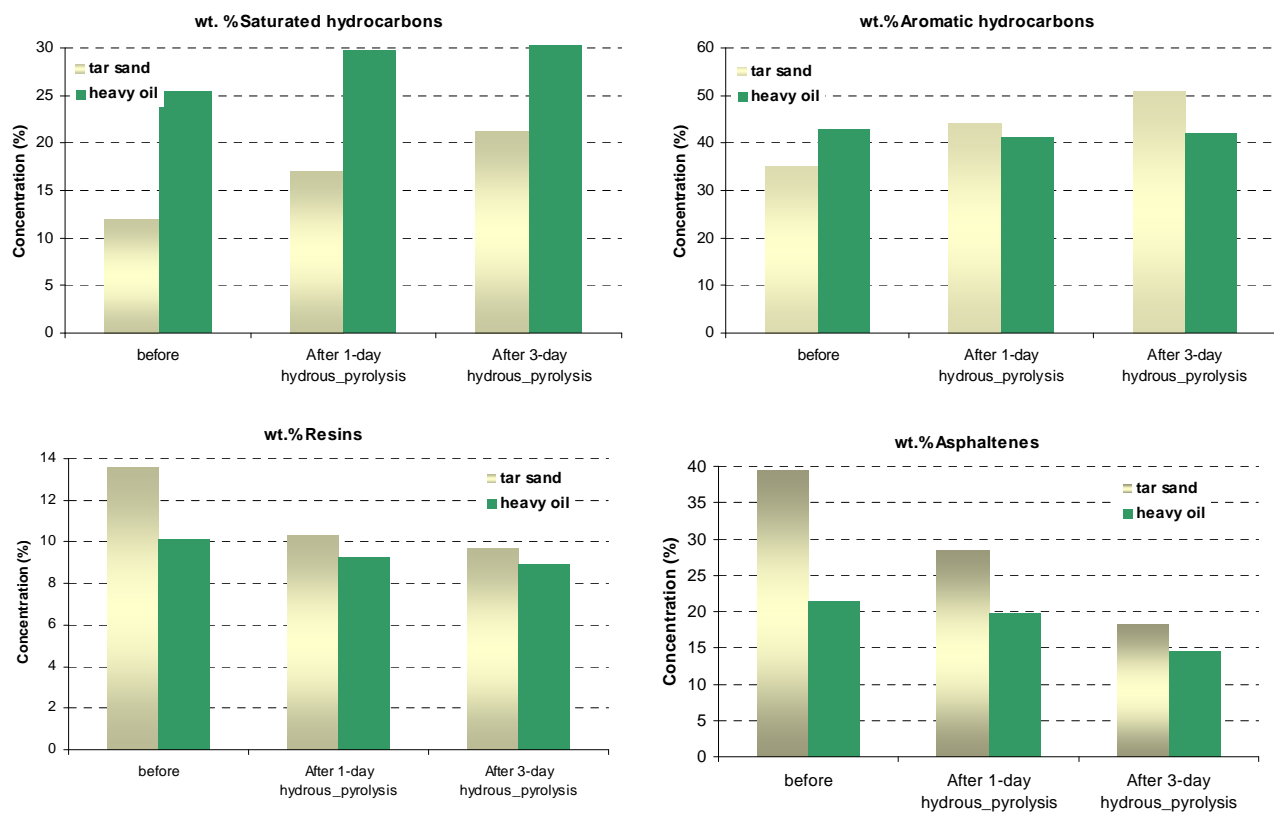


Figure 1: Saturated hydrocarbons, aromatic hydrocarbons, resin and asphaltene (SARA) composition of a heavy oil and an oil sand sample before and after 1 and 3 days of hydrous pyrolysis at 350°C.

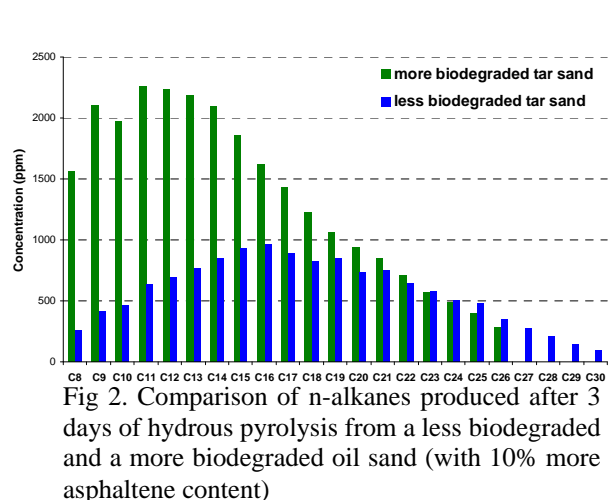


Fig 2. Comparison of n-alkanes produced after 3 days of hydrous pyrolysis from a less biodegraded and a more biodegraded oil sand (with 10% more asphaltene content)

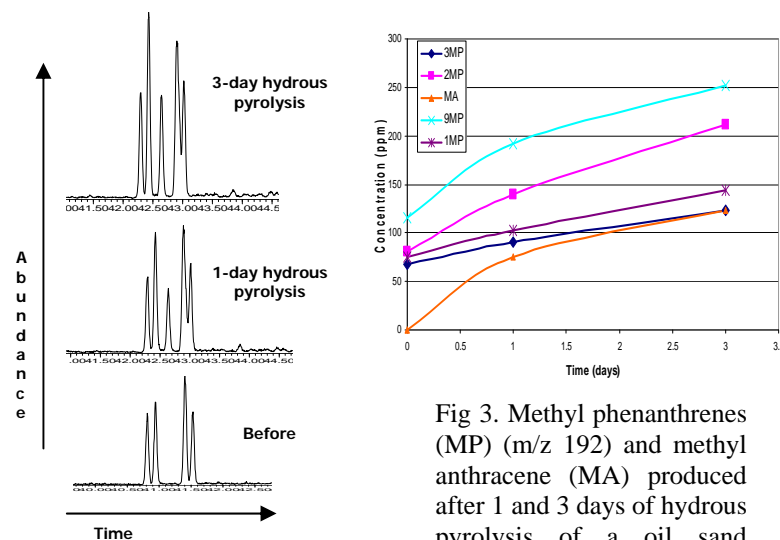


Fig 3. Methyl phenanthrenes (MP) (m/z 192) and methyl anthracene (MA) produced after 1 and 3 days of hydrous pyrolysis of a oil sand sample.

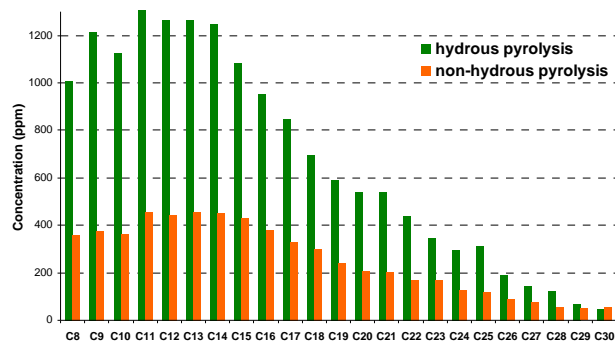


Fig 4. Comparison between n-alkanes produced during 1-day hydrous and non-hydrous (no added water) experiments of a severely biodegraded oil

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