Using Produced Oil Molecular Composition to Monitor In Situ Upgrading Operations in Oil Sands and Heavy Oil Reservoirs

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Summary

Upgrading of heavy oil and oil sands under simulated high temperature thermal recovery reservoir conditions was conducted to evaluate mechanisms and sources of the produced light hydrocarbon compounds that directly affect oil fluid properties as well as the identification of geochemical proxies to monitor in situ upgrading operations. The main results suggest that the polar fractions (resins and asphaltenes) are the main source of the light hydrocarbons produced during the simulated upgrading process. The neoformation of novel compounds such as alkylanthracenes and alkylbenzothiophenes in our experiments and their observed formation in oils from current generation thermal recovery SAGD pilots suggests some molecular changes are suitable to monitor steaming effects under current thermal recovery conditions from analysis of produced oils, as well as monitoring more dramatic changes under high temperature in situ upgrading conditions.

Introduction

The world oil inventory is dominated by heavy oils and oil sand bitumens generated almost entirely by the process of biodegradation of conventional oil over geological timescales (Roadifer, 1987). These oils are difficult to produce and transport because of their high viscosity (Larter et al., 2008). Reservoir heating by steam or electricity and/or solvent injection to mobilize the oil is often essential in very heavy oil and oil sand recovery. During in-situ thermal recovery processes the injected steam heats the crude oil or bitumen and lowers its viscosity allowing it to flow. Viscosity reduction with increasing temperature is regarded as a proven mechanism for very heavy oil recovery since the viscosity decreases over several orders of magnitude when the temperature is raised to 200 ºC. Heat from steam injection can also effect very minor changes in the chemical composition of the oil but employing catalysts in the reservoir and increasing temperatures above steam temperature during in-situ upgrading of heavy oil and bitumen may enable a more desirable product to be produced within a short timescale. However, there is currently no system established to monitor the chemical processes in-situ during thermal recovery or in situ upgrading where heat hydrogen, water, catalysts and oil all interact in a complex natural reactor. A detailed knowledge of the molecular transformation undergone by heavy oil and bitumen under in-reservoir thermal or catalytic processing allows the chemical composition of the produced oil to be used as a natural tracer to monitor the progression of the steam or upgrading front in the subsurface. The present study describes the changes caused by various reactions occurring during steam injection simulation. We look at the impact of heating

oil sands with water under conditions that might ensue in an in-situ process where heat is applied to the reservoir via superheated steam, electrical heating or in-situ combustion where water is present.

Method

Heavy oil and oil sands core samples were processed under hydrous conditions at 250°C, 300°C and 350°C for time periods of up to seven days using regular water. Pyrolysates were analyzed for bulk and molecular composition. For molecular investigation, the total hydrocarbon fractions were isolated following de-asphaltening of the bitumen and heavy oil samples. GCMS analysis was 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.

Examples

The main results demonstrate that native oil sands bitumens are naturally characterized by a lack of n-alkane and isoprenoid alkane hydrocarbons and generate a relatively uniform pattern of n-alkanes up to C_{30} and isoprenoid alkanes such as pristane and phytane, under high temperature simulated thermal recovery conditions (over 300ºC, Figure 1). The generation of tricyclic condensed aromatic hydrocarbon molecules, some of which are not present, or are at very low concentration in the original oil sand, appear to be good indicators of the progress of thermal conversion. For instance, the production of alkylanthracenes follows pseudo apparent first-order kinetics allowing the calculation of pseudo rate constants (Figure 2). Such parameters can be used to track process oil temperature histories.

The evaluation of some molecular parameters traditionally used to monitor thermal stress in basin settings and also recently proposed as proxies for in reservoir process monitoring (Bennett et al., 2008), suggests that those parameters based on biomarker ratios are probably suitable to be used as proxies for thermal conversion in procedures with temperatures below approximately 300ºC. Under the most extreme experimental conditions (350ºC) biomarkers such as monoaromatic and triaromatic steroids and the saturated hydrocarbon biomarkers are destroyed or diluted with time. The neo-production of adamantanes is also good reaction proxy as well.

Bitumen reactivity in the aqueous environment at temperatures below 300ºC seems to be low; however, we have shown that neoformation of compounds such as alkylanthracenes, not abundant in unaltered oils (0 - 3 ppm), at thermal recovery conditions suggests some molecular changes are suitable to monitor steaming effects under current thermal recovery conditions. As an example, figure 3 shows a SAGD produced oil depicting generated methylanthracene (about 10 ppm), compared to a sample upgraded after simulated steam recovery at 350 ºC. Alkybenzothiophenes are also produced under SAGD conditions. In general, during simulated thermal recovery experiments the oil asphaltene fraction decreases, but resins do not show such large variations on absolute quantification even though FTMS analysis indicate changes in this fraction are occurring.

The results suggest that the asphaltene and resin fractions are probably the major 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 (Ignasiak et al., 1977; Payzant et al., 1979; Rubinstein et al., 1979; Rubinstein and Strausz, 1979; Strausz et al., 1992). The principal proposed mechanisms are cracking of side chains from aromatic groups and cracking of aliphatic fragments linked through heteroatoms in cyclic systems. Temperature and heating times are the dominant control factors on hydrocarbon yields as indicated by higher yields with longer heating time and

dramatically increasing yields occurring at 350 ºC pyrolysis temperature. The amount and properties of hydrocarbons formed during the thermal reactions may also be significantly influenced by the nature and composition of the starting oil which shows very significant variations across the Albertan heavy oil province.

Conclusions

The results of simulated thermal recovery experiments (under non catalytic steam recovery conditions) suggest that the asphaltene and resin fractions are probably the main source of the newly formed saturated and aromatic hydrocarbons. The principal proposed mechanisms are cracking of side chains from aromatic structures in resins and asphaltenes and cracking of aliphatic fragments linked through heteroatoms in cyclic systems present in the asphaltene molecular structure.

Neoformation of compounds such as alkylanthracenes at thermal recovery conditions, components absent or not abundant in unaltered oils, suggests some molecular changes are suitable to monitor steaming effects under current thermal recovery procedures. Monitoring of all fluid compositions prior to and during a recovery operation assist in optimizing recovery and reducing costs and are thus recommended.

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.

Acknowledgements

References

Bennett, B., Larter, S.R., Carbognani, L., Pereira-Almao, P., 2008. Identification and characterization of reaction proxies for monitoring the progress of thermal processing of heavy oils and tar sands under vis-breaking conditions. Energy & Fuels 22, 440-448.

Ignasiak, T., Kempjones, A.V., Strausz, O.P., 1977. The molecular structure of Athabasca asphaltene. Cleavage of carbon-sulfur bonds by radical ion electron-transfer reactions. Journal of Organic Chemistry 42, 312-320.

Larter, S., Adams, J., Gates, I.D., Bennett, B., Huang, H., 2008. The origin, prediction and impact of oil viscosity heterogeneity on the production characteristics of tar sand and heavy oil reservoirs. Journal of Canadian Petroleum Technology 47, 52-61.

Payzant, J.D., Rubinstein, I., Hogg, A.M., Strausz, O.P., 1979. Field-Ionization Mass-Spectrometry - Application to geochemical analysis. Geochimica et Cosmochimica Acta 43, 1187-1193.

Roadifer, R.E., 1987. Size distributions of the world's largest known oil and tar accumulations. Exploration for Heavy Crude Oil and Natural Bitumen 25, 3-23.

Rubinstein, I., Spyckerelle, C., Strausz, O.P., 1979. Pyrolysis of Asphaltenes - Source of Geochemical Information. Geochimica et Cosmochimica Acta 43, 1-6.

Rubinstein, I., Strausz, O.P., 1979. Thermal-Treatment of The Athabasca Oil Sand Bitumen and Its Component Parts. Geochimica et Cosmochimica Acta 43, 1887-1893.

Strausz, O.P., Mojelsky, T.W., Lown, E.M., 1992. The Molecular-Structure of Asphaltene - An Unfolding Story. Fuel 71, 1355-1363.
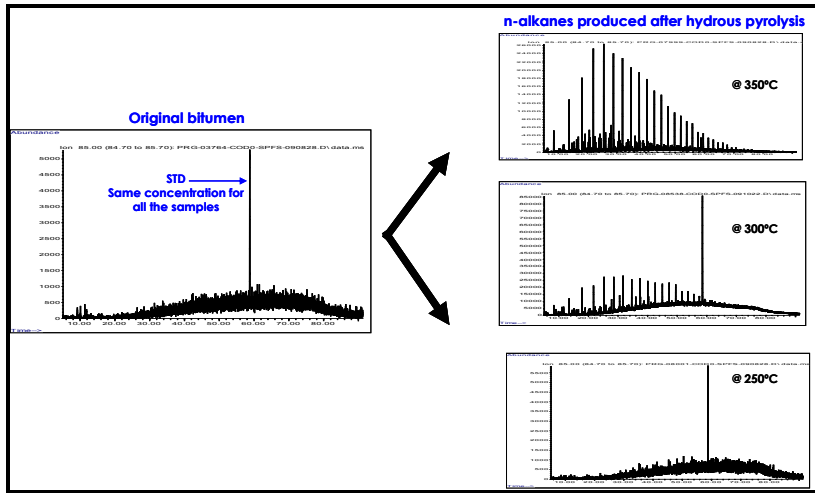
Figure 1: Mass chromatogram m/z 85, depicting the generation of n-alkanes after hydrous pyrolysis @ 300 - 350ºC. For most oil sand pools, where n-alkanes have been totally removed by biodegradation, the production of new n-alkanes may allow the monitoring of the progress of the upgrading front in high temperature thermal recovery procedures (>>250ºC)
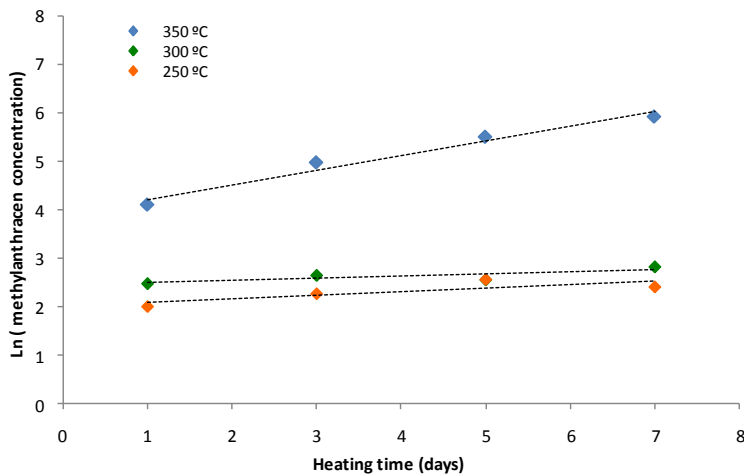
Figure 2: Production of methylanthracene with time, after up to 7 days of hydrous pyrolysis @ 250ºC, 300ºC and 350ºC. Concentration data is calculated using the ion m/z 192. The Ln of the concentration is used to illustrate the apparent first order pseudo kinetics of the formation of alkyl anthracenes.
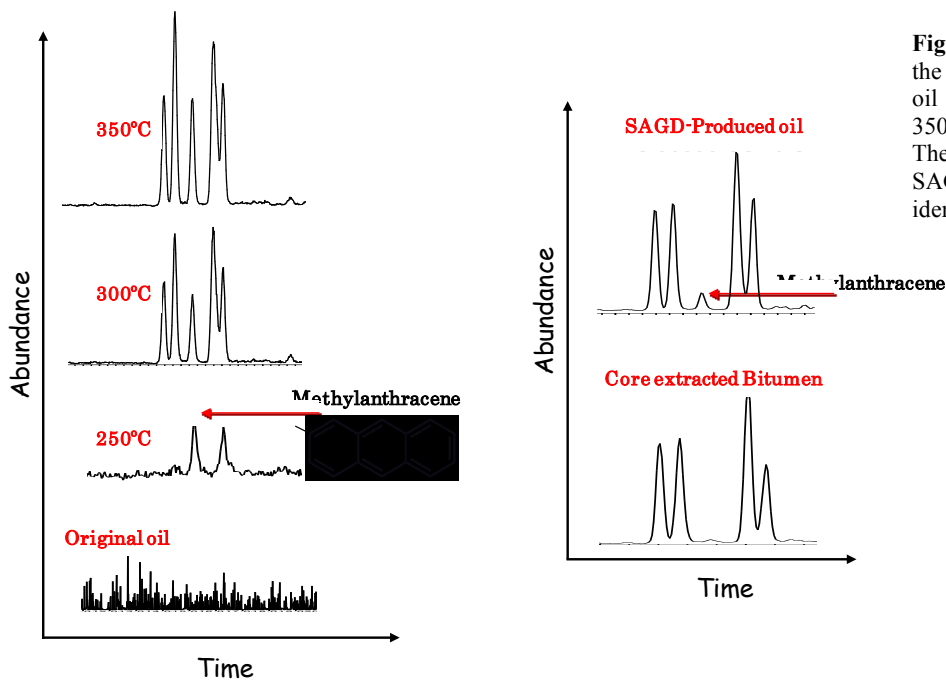
Figure 3: Mass chromatogram m/z 192, depicting the presence of methylanthracene in an upgraded oil after hydrous pyrolysis @ 250 ºC, 300 ºC and 350 ºC (left) and in a SAGD produced oil (right). The generation of methylanthracene is lower at SAGD conditions, but the peak is still easily identifiable.