

# EFFECT OF STEAM ON COKING CHEMISTRY OF ATHABASCA BITUMEN

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## INTRODUCTION

Fluid-coking is an important technology used in upgrading of bitumen and petroleum residues. The process uses a fluidized bed of hot coke particles to crack the feedstock. The bed is fluidized by steam, which also acts as a stripping medium to remove the distillate from the surface of the coke particles. Steam has long been thought of as chemically 'inert' in this process, in that it does not effect the product quality or yields. The use of other fluidizing media has been considered as an alternative to steam, including methane or nitrogen. Therefore, the question as to the chemical influence of steam is an important one and this study was undertaken to determine this on a micro-lab scale and on a larger pilot scale.

Much of the previous research into the effect of steam on hydrocarbons has been limited to the lower temperature regime associated with thermal maturation of kerogen in aqueous environments (<400°C). Research has focussed on hydrous pyrolysis experiments using kerogens and stable isotope analysis<sup>1,2</sup>. The chemical transformation of kerogen to bitumen, oil and gas has been studied to assess the role of water in these reactions. Studies at low temperatures (<150°C) conclude that water-hydrogen may exchange with certain labile organic hydrogen sites, e.g., those bound to nitrogen, sulfur and oxygen<sup>3</sup>. There is some evidence of hydrogen exchange with aromatic hydrogen and alkyl-hydrogen via carbonium ion mechanisms<sup>4,5</sup>. However, the higher temperatures of fluid-coking (530°C) and other upgrading processes, lead to free-radical reactions. Studies by Hoering<sup>6</sup>, Lewan<sup>7</sup>, and Stalker et al.<sup>8</sup>, have shown that at higher temperatures, exchange between water-hydrogen and organic-hydrogen is due to quenching of free organic radical sites. Thermodynamically, the reactions of steam and free-radicals have been shown to be favorable under certain reaction conditions<sup>9</sup>.

Song et al.<sup>9</sup> have studied the effect of water on the process of coal liquefaction. Water was seen to have three effects on liquefaction; chemical, physical and surface interactions. The increase in coal conversion was attributed to increased removal of oxygen functionalities in the presence of water, and therefore a reduction in retrogressive reactions. Tse et al.<sup>10</sup> suggested that water can reduce retrogressive reactions such as crosslinking of hydroxy groups. Siskin et al.<sup>11,12</sup> have observed that water may increase depolymerization by cleavage of ether linkages. Clark and Kirk studied the upgrading of bitumen with water at temperatures up to 415°C<sup>13</sup>. Their results show that water has an effect in decreasing insoluble material produced and also decreasing the sulfur content of the liquids produced. This enhancement of product quantity and quality was improved even further in the presence of an iron-based catalyst.

The objective of this research project was to determine the extent to which steam exchanges/donates hydrogen to the reacting bitumen molecules under coking conditions. Experiments were carried out with water doped with D<sub>2</sub>O to trace any exchanged deuterium atoms. Comparisons of experiments carried out with and without water were made to ascertain the effect that steam may have on coking chemistry.

## EXPERIMENTAL

The feedstock used in this study was Athabasca Bitumen obtained from Syncrude Canada. A 5.6 wt% solution of deuterium oxide (D<sub>2</sub>O) in water was used for all reactions. The coking reactions were carried out in 15 ml microautoclave reactors heated in a fluidized sand bath to temperatures in the range of 350-480°C. 3g of bitumen was accurately weighed into the reactor along with 0.6g D<sub>2</sub>O solution. The reactor was closed and purged with nitrogen to atmospheric pressure. For the reactions without D<sub>2</sub>O solution (dry), the nitrogen pressure in the reactor was increased to account for the pressure generated by steam in the reactions with water. The reactor was lowered into the sand bath for a pre-determined reaction time and then quickly quenched in cold water. Gases were vented from the reactor and analyzed for hydrocarbon composition by Gas Chromatography. The products in the reactor were extracted in toluene to give coke (toluene insolubles) and liquids (toluene solubles). The coke was dried and weighed to give coke yield. The liquids were analyzed by elemental analysis for C, H, N and S content. <sup>1</sup>H and <sup>2</sup>H liquid NMR were used to quantify the % deuterium in the liquid samples.

In order to determine the deuteration of bitumen under conditions more applicable to fluid coking conditions (530°C, fluidized bed, short residence time), the 3" coking pilot plant at Syncrude Research Center was utilized for two reactions. A 5% solution of D<sub>2</sub>O in water was used as the fluidizing medium. Liquid products were analyzed by NMR to give %D.

## RESULTS

In order to determine the extent to which steam changes the chemistry of the coking process, several analytical procedures were utilized. This section will show the major findings from each of these, followed by a discussion of the possible mechanism that can explain these changes.

**Coke Yield:** The yield of toluene insoluble material (coke) at various reaction times at 450°C is shown in Figure 1. The MCR of Athabasca bitumen is 14%. The figure shows that coke yield with and without water exceeds 20% after 60 minutes. This is because a closed reactor is used for this study. At 450°C, volatiles produced in the cracking of bitumen can further crack to produce gas or recombine to produce coke. In the presence of steam, coke yield is reduced from 24% to 21%.

**Gas Composition:** Figure 2 shows the hydrocarbon gas composition after bitumen coking at 450°C and 60 minutes reaction time. The most striking result is the reduction in methane produced when steam is used in the reaction. The presence of steam appears to reduce the cracking of alkyl-aromatics leading to a reduction in methane formation.

**Sulfur Analysis:** Figure 3 shows the wt% sulfur in the liquid products from bitumen coking at 450°C. Desulfurization of bitumen proceeds by thermal cleavage of C-S bonds (aliphatic sulfides). These bonds are relatively weak (compared to C-C bonds) and are therefore the first to crack, which is observed in that most of the desulfurization takes place in the first 10 minutes of the reaction. In the presence of steam, removal of sulfur is reduced.

**<sup>1</sup>H and <sup>2</sup>H Liquid NMR:** This technique was used to quantify the percentage of deuterium atoms per total hydrogen atoms (%D) in various liquid products from bitumen coking. The technique also shows the preferred position that exchanged deuterium will attach to bitumen and its products. Figure 4 shows an example of the <sup>2</sup>H spectra of bitumen liquid products detailing the areas used to quantify the data. The spectra has been split into 3 sections, namely aromatic protons,  $\alpha$ -CH<sub>2</sub> (benzylic) and  $\alpha$ -CH<sub>3</sub> protons (i.e., located on carbon atoms adjacent to aromatic rings), and  $\beta$ - and  $\gamma$ - protons (i.e., located on carbon atoms one and two positions removed from an aromatic ring). Figure 5 shows %D at various reaction conditions. The data shown at 530°C is from liquids taken from the Syncrude coking pilot unit discussed in the experimental section of this paper. It should be noted that in the control experiment (530°C, no D<sub>2</sub>O), the %D was 0.014% (natural abundance of deuterium is 0.015%). Exchange of deuterium atoms from D<sub>2</sub>O with organic protons from the bitumen occurs mostly at the  $\alpha$ -position. Aromatic and  $\gamma$ -carbon deuterations occur but to a lesser extent than  $\alpha$ -carbon deuteration

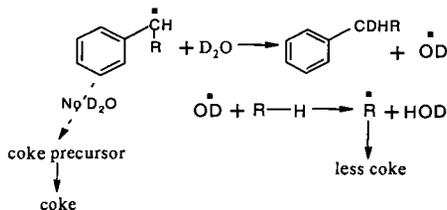
## DISCUSSION

The results show that steam is reducing coke yield, methane formation and sulfur removal. The most likely explanation of these observations is by considering radical-stabilization by water-hydrogen exchange. This will cause a reduction in radical-recombination reactions that will lead to coke, stabilization of alkyl-aromatic radicals leading to reduction in methane, and stabilization of C-S radicals leading to reduction in sulfur removal. A second stage of sulfur removal has also been postulated by Kakimura et al.<sup>14</sup>. Hydrothermal cracking of C-S bonds in aromatic structures led to increased removal of sulfur and reduction in viscosity. Based on the limited sulfur analysis taken in this study, it is impossible to back-up the ideas put forward by Kakimura. However, the data does agree with conclusions made previously when considering the coke yield and gas composition.

The data obtained by NMR of the liquid samples shows preferential exchange of deuterium at the  $\alpha$ -position (benzylic). This would be expected if conclusions from our previous results are correct, in that, water-hydrogen is stabilizing free-radicals in the coking process. Benzylic radicals are resonance-stabilized and are therefore more likely to exist as reactive intermediates in the coking reaction. Stabilization of these radicals can occur more readily and this is shown with the preferential deuteration of benzylic carbons. This hypothesis can be backed up when considering the coking reaction at 350°C. This reaction temperature does not give rise to many free-radicals (compared to >425°C) and the preferential deuteration of the benzylic position does not occur. The %D data obtained for the pilot plant data taken at 530°C does show a decrease in overall deuterium incorporation into the liquids due to the much decreased residence time of the bitumen cracking products in the reactor. The pilot unit also operates at a much lower pressure than the closed reactors used in the other experiments, which could also explain the decrease in deuteration. The results still show evidence for the radical stabilization behavior that is inferred from the results obtained at lower temperatures and in closed microautoclave reactors.

Figure 6 shows a comparison of the coke yield (divided by 100) and %D in the liquids produced under increasing reaction severity. The data shows that increasing reaction severity give increasing coke yield and an overall trend of increasing deuteration. The decrease at the highest severity conditions is probably due to excess hydrocarbon gas formation that will remove some of the deuterium from the liquid fraction. The relationship between coke yield and %D implies that a similar mechanism can account for the effect of steam on these two parameters.

**Proposed Mechanism:** Steam is changing the chemistry of the coking process by 'stabilizing' free-radicals that are produced by thermal cleavage of C-C and C-S bonds. This process of free-radical 'stabilization' has to be carefully defined. Free-radical 'capping' is a term that has been used to explain termination reactions by gas-phase hydrogen or hydrogen transferred from donor solvents<sup>15,16</sup>. This mechanism does not particularly apply to this system because the hydroxyl radical will tend to abstract a hydrogen from the bitumen. This concept of 'stabilization' is more applicable because it is possible that the radical produced in the stabilization of the hydroxyl radical will not recombine to produce coke.



**Scheme 1. Mechanism of 'stabilization' of free-radicals produced by cracking of bitumen**

## CONCLUSIONS

The purpose of this study was to find evidence for the chemical interaction of steam and bitumen under coking conditions. Through various analytical techniques, namely, coke yield, elemental analysis, gas analysis, and liquid NMR, the concept of free-radical stabilization by water-hydrogen has been explored. This free-radical stabilization process can also be inferred by comparing the gas composition and the liquids sulfur content for reactions with and without steam. Water is exchanging/donating hydrogen to the radicals to reduce methane formation and sulfur removal. NMR data has shown preferential deuteration of the benzylic carbons, which would suggest that free-radical stabilization is occurring (benzylic radicals are very stable). Coking reactions carried out in a pilot-unit under conditions similar to real fluid-coking conditions, show this preferential deuteration of the benzylic carbons and suggest that even with the short residence time and low pressures of fluid-coking, water-hydrogen may be exchanged/donated to the reacting bitumen.

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## REFERENCES

- Siskin, M. and Katritzky, A. R. *ACS, Div. Fuel. Chem. Prep.* 44(2), 324, 1999
- Lewan, M. D., *Geochim. Cosmochim. Acta.* 61, 3691-3723, 1997
- Koepp, M. in *Short papers of the Fourth International Conference, Geochronology, Cosmochronology, Isotope Geology*, 1978
- Alexander, R., Kagi, R. I., and Larcher, A. V., *Geochim. Cosmochim. Acta.*, 46, 219-222, 1982
- Werstiuk, N. H., and Ju, C., *Can. J. Chem.* 67, 812-815, 1989
- Hoering, T. C., *Org. Geochem.* 5, 267-278, 1984
- Stalker, L., Larter, S. R., and Farrimond, P. *Org. Geochem.* 28, 238-253, 1998
- Lewan, M. D., *ACS, Div. Fuel. Chem. Prep.* 44(2), 420, 1999
- Song, C., Saini, A. K., and Schobert, H. H., *Energy Fuels* 8, 301-312, 1994
- Tse, D. S., Hirschon, A. S., Malhotra, R., McMillen, D. F., and Ross, D. S., *ACS, Div. Fuel. Chem. Prep.* 36(1), 23, 1991
- Siskin, M., Katritzky, A. R., Balasubramanian, M., *Energy Fuels* 5, 770, 1991
- Siskin, M., Bron, G., Vaughn, S. N., Katritzky, A. R., Balasubramanian, M., *Energy Fuels* 4, 488, 1991
- Clark, P. D. and Kirk, M. J. *Energy Fuels* 8, 380-387, 1994
- Kakimura, H., Takahashi, S., Kishita, A., Moriya, T., Hong, C. X., and Enomoto, H., *ACS Div. Fuel. Chem. Prep.* 43(3), 741, 1998
- Curran, G. P., Struck, R.T., Gorin, E. *Ind. Eng. Chem. Proc. Des. Dev.* 6, 167, 1967.
- Wiser, W.H. *Fuel.* 47, 475, 1968

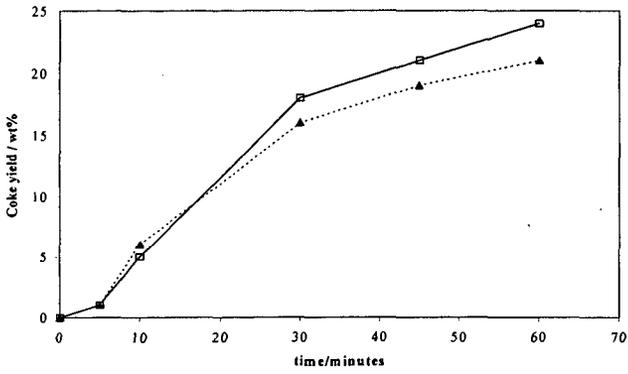


Figure 1. Effect of steam on toluene insoluble (coke) yield from bitumen coking at 450C (▲-steam; □-Dry)

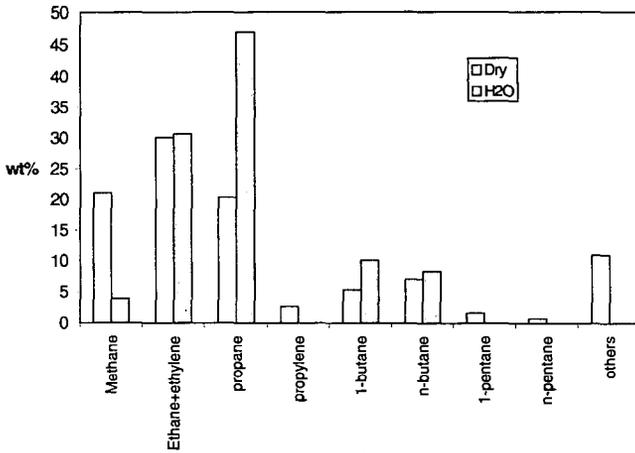


Figure 2. Hydrocarbon gas composition from bitumen coking at 450C and 60 minutes

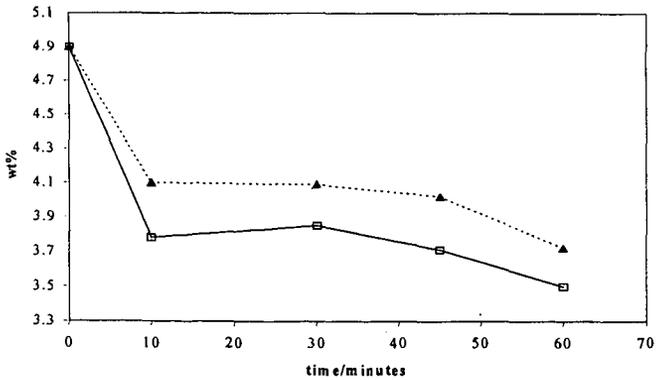


Figure 3. Sulfur content of liquid products from bitumen coking at 450C (▲-steam; □-Dry)

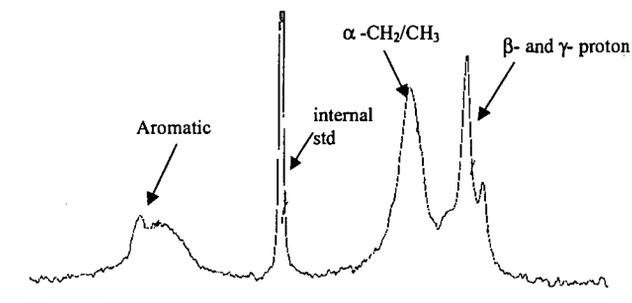


Figure 4.  $^1\text{H}$  NMR spectra of liquid products from bitumen coking – 450C 60min 5%  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$

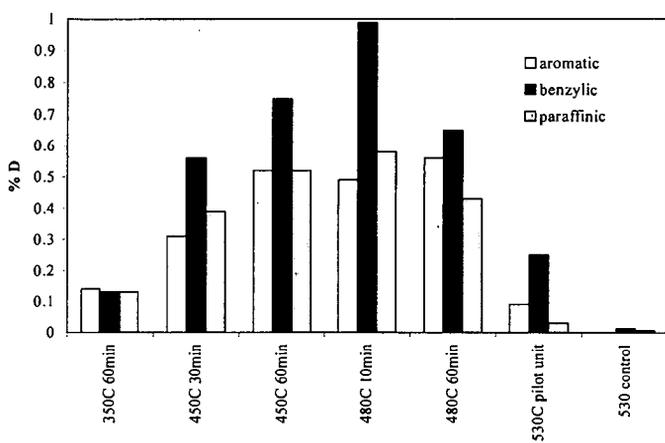


Figure 5. %D in liquid products from bitumen coking (5%  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$ )

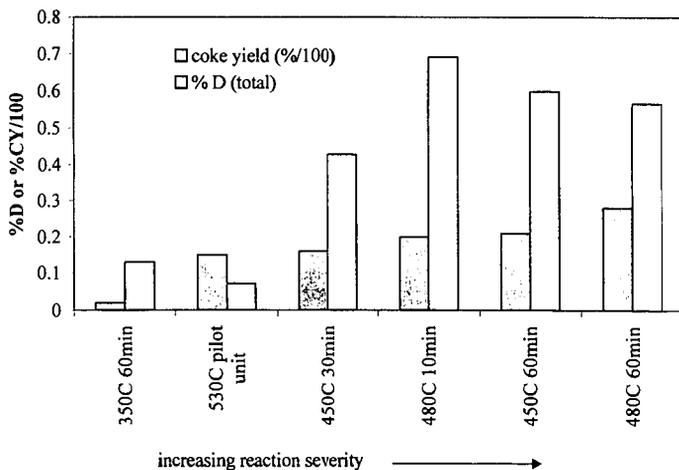


Figure 6. Comparison of %D in liquids and coke yield for bitumen coking at increasing severity