



# Role of metal halides in coke formation during bitumen upgrading



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## ABSTRACT

Metal chlorides are naturally present in bitumen. The concern of such metal chlorides in downstream processing is related to physical processes. However, a previous study revealed that mild bromination of asphaltene resulted in a product with increased hardness and that was insoluble in both aromatic and paraffinic solvents, like coke. It was then hypothesized that the naturally present metal chlorides could affect solids yield during thermal conversion. The hypothesis was investigated by performing thermal conversion of Athabasca vacuum residue at 400 °C for 1 h in the presence of 1 wt% of different metal bromides (NaBr, CaBr<sub>2</sub>, MgBr<sub>2</sub>, CoBr<sub>2</sub>, and ZnBr<sub>2</sub>). Metal bromides were chosen instead of metal chlorides because vacuum residue does not contain bromine and it would facilitate analysis. Control experiments were also prepared: i) conversion in the presence of a base (Mg(OH)<sub>2</sub>) and ii) conversion in the absence of a metal bromide and/or base. The results revealed that the presence of acidic metal bromides during thermal cracking increased solids yield. Formation of a hydrogen halide (irrespective of the type of the halogen composing the metal halide) is a required step for metal halides to contribute to coke formation. It was also observed that acidic metal bromides caused halogen transfer to solid and liquid products and that this transfer was not due to trapped metal bromide salts. Acidic metal bromides increased solid yield during conversion of Athabasca vacuum residue from 2.5 wt% to 4–10 wt%. The increase in solids yield and halogen transfer by thermal conversion in the presence of acidic metal bromides was suppressed by the addition of a base, but it was not eliminated. Thermal cracking in the presence of a base, Mg(OH)<sub>2</sub>, decreased overall solid yield.

## 1. Introduction

The onset and the extent of coke formation are key parameters in the design and operation of thermal upgrading technologies for bitumen, and heavy oils in general. Forming coke from high sulfur content bitumen, except for its utility as carbon rejection method, represents a loss of material. The sequence of steps that lead to coke formation was described [1]. Maintaining solubility of molecules in the bulk oil phase is central to delaying the onset of coke formation. The solubility of a molecule in the bulk oil phase was related to two main parameters, namely, hydrogen-to-carbon ratio and molecular mass [2]. Reactions that lead to a decrease in hydrogen-to-carbon ratio, and/or an increase in molecular mass, would likely hasten the onset of coke formation. Coking during the thermal upgrading of bitumen is described in literature by Gray [3] and Gray and McCaffrey [4] for example.

In previous work [5] it was found that mild halogenation caused the formation of solid compounds that were insoluble in both aromatic and paraffinic solvents. Coke formation would therefore be accelerated when oil was halogenated.

The chlorine content in mineral free Athabasca bitumen, which was the feed of interest in this study, was reported to be of the order 20 µg/g on an oilsand basis, i.e. around 200 µg/g on an oil basis [6]. No other halogens were found during trace element analysis of the oil. Most of the chlorine associated with oilsands bitumen is present in the mineral matter [6]. Chlorides are also present in the process water and are reported to be in the range 50–500 µg/g [7].

The mineral matter and process water is usually removed before the bitumen is upgraded. Even though most of the chloride salts are removed during desalting, about 0.5% of salts remain coated with asphaltene in the diluted bitumen after the desalting process [3]. The impact of these salts in bitumen upgrading is described in terms of fouling and corrosion caused by the formation of hydrochloric acid (HCl). Hydrochloric acid is formed through the hydrolysis of the salts or by reaction of the salts with naphthenic acids present in the oil (Fig. 1) [3].

When hydrochloric acid is formed, it can react with thioethers (organic sulfides) to produce thiols (mercaptans) and organo-halides, although thioethers are generally less reactive to such cleavage than ethers [8]. Another possible pathway to organo-halides is by

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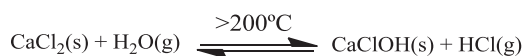


Fig. 1. HCl formation through the hydrolysis of native metal chlorides or through the reaction with naphthenic acids [3]

electrophilic addition of hydrochloric acid after acid catalyzed elimination of thiols. Likewise, addition of hydrogen halides to cracked products can occur. Conceptually it is therefore possible to imagine reaction pathways from metal chlorides to organo-halides during bitumen upgrading, and it is suspected that the naturally present metal chlorides could promote coke formation.

Following this type of chemistry in a complex matrix, such as bitumen, is difficult. It was therefore decided to pose the research question in such a way that it is analytically tractable: Can the naturally present metal chlorides salts increase coke formation? Additionally it was also of interest to determine whether the products from thermal conversion in the presence of metal halides were meaningfully different from the products from thermal conversion in the absence of metal halides.

In order to investigate this question, a vacuum residue fraction from Athabasca bitumen was thermally processed in the presence and absence of different metal bromides. Since the originally present metal halides in vacuum residue are metal chlorides, the choice of metal bromides should be explained. Since vacuum residue does not contain any bromine it would facilitate the tracking of the added halogen during thermal conversion. The metal halides tested were neutral ( $\text{NaBr}$ ) or acidic ( $\text{CaBr}_2$ ,  $\text{MgBr}_2$ ,  $\text{CoBr}_2$ , and  $\text{ZnBr}_2$ ) in nature. One basic metal hydroxide ( $\text{Mg}(\text{OH})_2$ ) was included as control.

## 2. Experimental

### 2.1. Materials

The feed material was a vacuum residue (VR) cut from Athabasca oilsands bitumen, which was supplied by Syncrude Canada Ltd. The VR cut was the  $> 575^\circ\text{C}$  boiling material and selected properties are given in Table 1. The chemicals used in this study are listed in Table 2.

### 2.2. Equipment and procedure

Thermal cracking reactions of VR in the presence or absence of metal bromides and/or base were performed in a Swagelok 316 stainless steel micro batch reactor (1 inch inner diameter and 5.5 inches long). As mentioned in the introduction, bromides were chosen instead of chlorides to facilitate identification during analysis. Approximately 6 g of VR was crushed while frozen, followed by the addition of 1 wt% (0.06 g) of metal bromide and/or base; the mass of the metal bromide and/or base included the crystal water. In one set of experiments a mixture of  $\text{MgBr}_2$  (0.06 g) and  $\text{Mg}(\text{OH})_2$  (0.06 g) was employed.

The mixture was placed in a glass vial that was placed in the micro reactor. The glass vial avoids contact between the sample and the metal wall of the micro-reactor. The micro-reactor was purged with nitrogen gas and it was placed in a fluidized sand bath (SBS-4 from Techne) for 1 h at  $400^\circ\text{C}$ . Before reaction, the micro reactor was purged with nitrogen and a leaking test was performed. The reactions were performed under autogenous pressure. After the reaction time, the reactor was allowed to cool down to room temperature ( $\sim 23^\circ\text{C}$ ) and the gas was released in the fumehood. Gas weight was obtained by weighing the closed and still pressurized micro reactor before and after reaction, as well as after gas release. The gas yields for all experiments were in the range 1–5 wt% based on the VR feed (Table 3); the gaseous products were not further analysed. Liquid and solid products were recovered by

Table 1  
Characterization data of Athabasca VR feed material.

Description	Athabasca VR feed	
	x	s
Density ( $\text{kg}/\text{m}^3$ ) <sup>a</sup>	1066.5	2.7
Density ( $\text{kg}/\text{m}^3$ ) <sup>b</sup>	1067.1	
Elemental analysis <sup>c</sup>		
Carbon	81.25	0.35
Hydrogen	9.28	0.12
Nitrogen	0.72	0.00
Sulfur	5.62	0.01
TGA <sup>d</sup>		
Onset of mass loss ( $^\circ\text{C}$ )	395.6	1.1
Micro carbon residue (wt%) <sup>a</sup>	18.2	0.3
Micro carbon residue (wt%) <sup>c</sup>	16.8	0.3
Mineral matter (wt%)	1.41	0.08
Metals content (ppm) <sup>d</sup>		
Ni	165	11
V	312	3
Ca	425	127
Fe	2143	293
Zn	100	16

<sup>a</sup> Determined experimentally.

<sup>b</sup> Calculated from elemental analysis.

<sup>c</sup> Average (x) and standard deviation (s) of analysis in duplicate are reported.

<sup>d</sup> Average (x) and standard deviation (s) of analysis in triplicate are reported.

<sup>e</sup> Calculated mineral matter free micro carbon residue.

adding toluene into the glass vial.

The recovered liquid and solid products were transferred to a 50 mL Teflon tube. The Teflon tube was then centrifuged in a Sorvall RC6 centrifuge at 18300 rpm for 15 min at  $4^\circ\text{C}$ . The supernatant was transferred to a boiling flask and toluene was evaporated by using a rotary evaporator (Heizbad Hei-VAP from Heidolph) at  $44^\circ\text{C}$  and 70 mbar pressure. The recovered liquid was analysed by X-ray fluorescence (XRF), elemental analysis, Fourier transform infra-red (FTIR), refractive index, and thermal gravimetric analysis (TGA). Solid material was recovered and washed with 500 mL Milli-Q water by using a vacuum filtration system. Metal bromides and hydroxides were dissolved in water and the solid material (including some toluene insolubles) was recovered for analysis. All reactions were performed in triplicate.

Control samples without addition of metal bromides were obtained by following the same procedure.

### 2.3. Analyses

The density of pure toluene and of VR feed diluted in toluene was measured in a density meter from Anton Paar, model DMA 4500 M at a controlled temperature of  $25^\circ\text{C}$ . The density of VR was determined in a 50% toluene solution and the density of the pure VR was obtained by calculation based on mass (m) and density ( $\rho$ ) using Eq. (1) (the density of pure toluene obtained from the density meter was  $862.32 \pm 0.01 \text{ kg}/\text{m}^3$ ).

$$\rho_{\text{MIXTURE}} = \frac{m_{\text{VR}} + m_{\text{TOLUENE}}}{\frac{m_{\text{VR}}}{\rho_{\text{VR}}} + \frac{m_{\text{TOLUENE}}}{\rho_{\text{TOLUENE}}}} \quad (1)$$

The density of the VR was also determined indirectly from the elemental analysis (Table 1) of the VR by calculation using Eq. (2), where H, S and N refer to the mass fraction of each element [3].

$$\rho_{\text{VR}} = 1033 - 13.69H + 13.85S + 115.7N \quad (2)$$

Elemental analyses were performed elsewhere using a Carlo Erba Elemental Analysis EA1108 Analyser. Only one sample from each treatment was analysed in duplicate.

Fourier Transform Infrared (FTIR) analysis was performed using an ABB MB3000 equipped with a Pike MIRacle Attenuated Total Reflectance attachment. Spectra were collected at a resolution of

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