

UPGRADING OF ALBERTA HEAVY OILS BY SUPERACID-CATALYZED HYDROCRACKING

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Keywords: bitumen, asphaltene, hydrocracking, superacid

INTRODUCTION

An alternative to conventional catalytic hydrocracking of tar sand bitumens would be a superacid-catalyzed hydrocracking. Olah *et al.*¹ have shown the superacid HBF₄ to be an excellent catalyst at low temperatures (105–170°C) and hydrogen pressure (500 psi) for the depolymerization/liqefaction of coal. Superacids prepared from anhydrous HF and metal halides (e.g. TaF₅)² and Lewis acids³ have also been used for the catalytic hydrocracking of petroleum. However, HBF₄, with activity function⁴ $H_0 \sim -16$, offers the unique advantage, in addition to being non-reducible (hence would not oxidize products), of being a gas and readily falling apart to HF and BF₃, thus permitting the corrosive superacid components to be easily removed from the liquefaction/reaction mixture.

In Olah¹ *et al.*'s papers on the superacid treatment of coal, no product analysis data were reported. A study, however, was published on model compounds thought to represent the molecular bridging groups holding coal "monomers" together. Dibenzyl, diphenylmethane and biphenyl (along with their ether and sulfide analogs) were used. Under superacid conditions near quantitative conversions to products such as benzene, toluene, anthracene, p-xylene (phenol, benzenethiol) were obtained in high yields.

The aim of the present exploratory study was to assess the feasibility of employing HBF₄ for the depolymerization/hydrogenation of tar sand bitumens and asphaltenes. The characteristic features of this process can be summarized as follows:

- it involves ionic mechanisms, in contrast to the free radical mechanisms in thermocatalytic cracking and therefore may produce different, possibly more valuable, products than those obtained from the latter reactions;
- the temperature and hydrogen pressure required are much lower than in conventional hydrocracking;
- a gaseous catalyst is free of all the problems associated with solid catalysts (poisoning, core plugging, recovery);
- both HF and BF₃ can be readily separated from the product oil by distillation and recycled;
- neither HF nor BF₃ would cause any oxidative degradation of products; and
- the process is free of fluorine incorporation into products.

EXPERIMENTAL

Hydrocracking was done on 2.0–5.5 g samples of Athabasca or Cold Lake bitumen or asphaltene. Mixtures of the sample with 0–30 mL dry methylcyclohexane were placed in a 250-mL Parr autoclave under a dry nitrogen atmosphere. The autoclave was cooled to –78°C (in a dry ice-acetone bath) and 50-mL anhydrous HF was added. The vessel was closed tightly, warmed to room temperature and 500 psi BF₃ was introduced, followed by 500 psi H₂. Then the autoclave was heated to the desired reaction temperature and maintained at that temperature for 2–24 h. At the conclusion of the reaction, the autoclave was cooled to room temperature, depressurized, opened and the contents quenched with 500-mL ice water. The organic layer was separated and washed several times with a 10% sodium bicarbonate solution to remove traces of acid. The acid-free organic layer was then analyzed by conventional class separation and in some cases by capillary GC–MS, FTIR and ¹H and ¹³C NMR spectroscopy.

RESULTS AND DISCUSSION

The HBF₄-catalyzed hydrocracking of Athabasca bitumen (5.5 g) was carried out in a 24-h reaction at 170°C using, as in all subsequent experiments, 50-mL HF and 500 psi pressure each, BF₃ and H₂. The reaction yielded 33.0% *n*-pentane solubles, 14.7% CH₂Cl₂ solubles ("asphaltene") and 1.8% CH₂Cl₂ insolubles, indicating the formation of 50.5% volatiles (which were not recovered). This experiment demonstrated the high efficiency of the HBF₄ + H₂ superacid system in causing deep-rooted chemical alterations in the bitumen. The extent of the alterations can be appreciated by keeping in mind that in thermocatalytic hydrocracking at 170°C practically no reaction would occur and the yield of volatiles would be only a few percent.

In previous studies on coal liquefaction Olah *et al.*¹ used methylcyclohexane (MCH) as a solvent and hydrogen transfer agent thought to facilitate the process. For this reason, in a series of experiments the effect of added MCH on the hydrocracking of Athabasca bitumen and asphaltene was next examined. The percentage recoveries of bitumen, maltene and asphaltene from the reactions are presented in Figure 1 and Table 1. The data show that under the reaction conditions indicated in Table 1, increasing the volume of added MCH increases the yield of recovered products: bitumen, maltene and asphaltene. The only exception is the asphaltene from

the hydrocracking of asphaltene with 30-mL MCH. Total product yields above ~20-mL MCH exceed the amount of the initial feedstock from both bitumen and asphaltene and rapidly rise with further amounts of MCH. Thus, it is clear that the excess amount of products must be coming from the reactions of added MCH. Since neat MCH does not appear to react under similar reaction conditions, it must be concluded that the intermediates in the HBF₄-catalyzed hydrocracking of bitumen or asphaltene serve as initiators of the decomposition of MCH. At less than 5 mL, MCH does not appear to decompose or affect the hydrocracking of the bitumen or asphaltene feedstocks, except perhaps by the suppression of the small amount (1.8%) of coke which forms in long reactions. Five-mL MCH in short runs (≤ 2 h) and 30-mL MCH in long runs (24 h) suppressed formation of coke. Product yields with 5-mL MCH are about the same as without MCH.

Table 1. Superacid Treatment of Athabasca (Suncor Coker Feed) Bitumen and Asphaltene. Effect of the Quantity of Added MCH.

MCH (mL)	Asphaltene		Maltene	
	% recovered	% of starting material	% recovered	% of starting material
Bitumen				
5	18.5	8.1	81.5	35.7
15	13.1	9.4	86.9	62.3
30	5.8	11.7	94.2	191.6
Asphaltene				
5	57.1	44.6	42.9	33.5
15	54.6	49.2	45.3	40.8
30	19.1	38.4	80.9	161.6

^a 500 psi H₂, 500 psi BF₃, 50-mL HF, 1 h, 190°C, reactor volume 250 mL, sample size 2.5–3.1 g. ^b The asphaltene content of the bitumen was 15.5%.

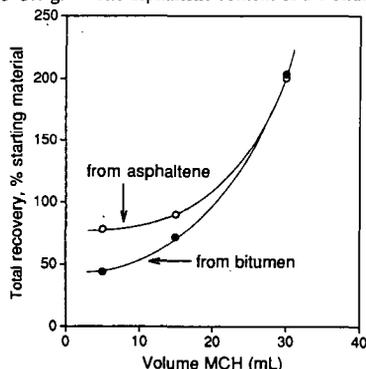


Figure 1. Product (bitumen) yields as a function of added MCH

The low yield of recovered products, Figure 1, in the reactions with 5-mL added MCH represents high conversions to volatiles, 56% from bitumen and 22% from asphaltene. At the same temperature, 190°C and 1-h reaction time, practically no decomposition takes place. With asphaltene, along with the volatiles, 30% conversion to *n*-pentane solubles also occurred. The results obtained from experiments with added MCH further validate the result obtained in the neat bitumen hydrocracking reaction.

Before progressing further, it is noted here that in the early stages of the investigations considerable difficulties were experienced with the lack of reproducibility. Moreover, it was noted that the maltene product—especially from the asphaltene reactions with added MCH—was highly reactive and upon exposure to air it reacted with oxygen, transforming the colorless mobile liquid oil to a translucent gum. This observation suggested that conjugated alkenes may have been produced, providing a possible explanation for the lack of reproducibility. Next, it was found that the fresh maltene product from the hydrocracking of Cold Lake bitumen contained no oxygen, but after two days' exposure to air the oxygen content was 5.8%.

Comparison of the IR spectra of air-protected and air-exposed samples, Figures 2 and 3, revealed the absence and presence of intense carboxylic (1705 and 3440 cm⁻¹) and possibly alcoholic (1080 cm⁻¹) group absorptions and the presence and absence of conjugated triene absorptions (1500–1700 cm⁻¹). It was also found that the double bonds could be readily brominated. Oxidation with *m*-chloroperbenzoic acid converted the "saturate" fraction to some polar material in >98% yield, suggesting the absence of any paraffinic hydrocarbons.

Furthermore, the GC of the "saturate" fraction featured two broad humps superimposed by a large number of peaks corresponding to individual compounds. Four of six selected major

peaks from GC-MS could be assigned to isomers of a $C_{16}H_{24}$, and the remainign two to some $C_{17}H_{26}$ hydrocarbons. These structures possess five C=C double bond equivalents. Next, in order to determine the number of double bonds in these structures, the "saturate" fraction was subjected to PtO_2 -catalyzed hydrogenation which led to chemical changes. It is known that tetra-substituted double bonds are not affected under these conditions.

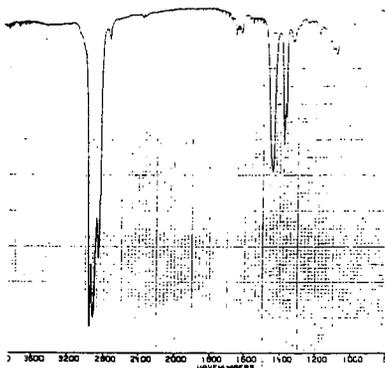


Figure 2. Infrared spectrum of the "saturate" fraction of Cold Lake superacid-treated asphaltene, stored under nitrogen.

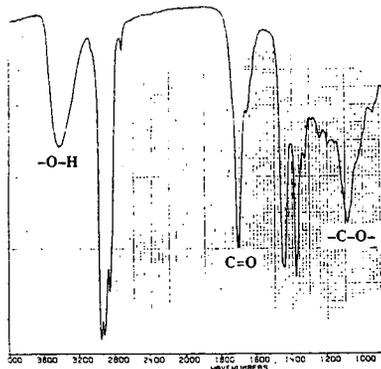
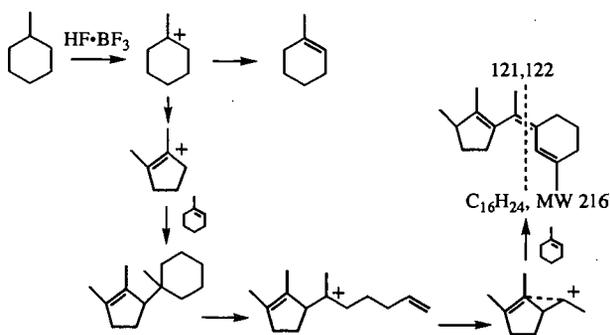


Figure 3. Infrared spectrum of the "saturate" fraction of Cold Lake superacid-treated asphaltene, exposed to air.

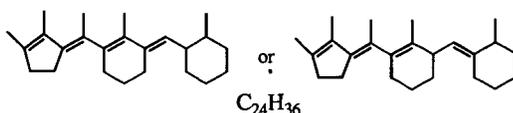
The 1H NMR spectrum of the "saturates" consisted almost entirely of aliphatic hydrogens with a small contribution from alkene hydrogens. The ^{13}C NMR spectrum showed significant signals in the 125–135 ppm range which are due to alkene carbons and from the attached proton test it appeared that the carbons resonating in the 125–135 ppm range had no attached hydrogens. This suggests that, in agreement with the 1H NMR spectrum, the resonances correspond to tetra-substituted alkenes.

In an attempt to obtain further structural information, the "saturate" fraction was subjected to ionic hydrogenation ($(Et)_3SiH$, CF_3CO_2H , $BF_3 \cdot Et_2O$, $0^\circ C$, 1 h) which, after alumina chromatography, gave ~35% yield of hydrogenated product. GC-MS analysis of this material showed that the $C_{16}H_{24}$ and $C_{17}H_{26}$ compounds in ionic hydrogenation were converted to $C_{16}H_{30}$ and $C_{17}H_{32}$ compounds, both of which contain two saturated rings. Therefore, the original $C_{16}H_{24}$ and $C_{17}H_{26}$ compounds each contained three carbon-carbon double bonds which must have been conjugated in order to account for the high reactivity of these molecules, as manifested by their spontaneous rapid reaction with atmospheric oxygen. Moreover, from the NMR spectra it is clear that the alkene carbons are quaternary. Therefore, we are forced to conclude that under the experimental conditions of the superacid-catalyzed hydrogenation employed, the MCH solvent undergoes ionic rearrangement, degradation and oligomerization. Speculative structures and mechanisms for the formation of the bicyclic conjugated quaternary tri-olefins are shown in Scheme 1.



Scheme 1. Superacid-catalyzed solvent polymerization

Most of the peaks in the GC-MS of the "saturate" fraction correspond to molecules with structures analogous to the $C_{16}H_{24}$ and $C_{17}H_{26}$ compounds. Thus, for example, in the chemical ionization GC-MS of the "saturate" fraction three major selected peaks corresponded to isomeric $C_{24}H_{36}$ compounds which would fit the tricyclic conjugated tetra-alkene structure



Thus, the C_{24} compounds appear to be the homologs of the C_{16} and C_{17} compounds having one more MCH ring, with or without an extra carbon atom.

The results from studies on the $HF\cdot BF_3$ -catalyzed hydrocracking in the presence of MCH point to the general reactivity of the $HF\cdot BF_3$ superacid system indicating that acyclic and cyclic hydrocarbons can be attacked. Indeed, the typical gas chromatograms of the saturates from the native bitumens displaying the series of biological markers are altered beyond recognition after the hydrocracking process (suggesting the destruction of cheilanthanes, hopanes, isoprenoids, etc.). Also, the monoaromatic subfraction after hydrocracking appears to be rich in 1-phenyl, 2,2-dimethyl-*n*-alkanes, whereas in the native asphaltene the aromatic-attached alkyl groups are *n*-alkyl, and branched alkyls are hardly present. The appearance of these products is consistent with the known tendency of superacids to catalyze the break-up of alkyl chains and bring about their isomerization to *t*-butyl structures. Superacids also catalyze the transalkylation of aromatic compounds which, together with the above isomerization reactions, could account for the generation of the branched alkyl products.

SUMMARY AND CONCLUSIONS

- It has been established that the superacid $HF\cdot BF_3$ is a highly effective catalyst for the hydrocracking of bitumens and asphaltenes even under very mild conditions (170–190°C, 1 h or less);
- The reactions involved proceed with ionic mechanisms as opposed to the free radical mechanisms in thermal hydrocracking, resulting in deep-rooted alterations of the chemical composition of the bitumen, evidenced by the high (56%) conversion of the bitumen to volatiles, the drastic changes in the gas chromatograms of the various compound classes of the bitumen and the appearance of many prominent branched alkylbenzene peaks, etc.
- In asphaltene, parallel to depolymerization some secondary polymerization leading to the formation of asphaltene-like materials takes place upon prolonged reaction times. Therefore, establishing the optimal reaction time is essential to obtain the most favorable conversions.
- Methylcyclohexane exhibits high reactivity with respect to the $HF\cdot BF_3$ superacid under the conditions of the bitumen or asphaltene hydrocracking process—typifying the general reactivity of cycloalkanes—resulting in the oligomerization of methylcyclohexane to produce conjugated alkenes; this reaction also reflects some of the possible ways by which the superacid may react with the bitumen or asphaltene since both these materials are known to contain cycloalkane units.
- Fluorine incorporation into the bitumen does not take place and no evidence could be found for catalyst consumption.
- BF_3 is a gas and HF a low-boiling liquid (b.p. 20°); both are highly water-soluble and therefore should be readily separable from the hydrocracked bitumen and recycled for further use. Thus, taking the above results in conjunction with the ready recoverability of the catalyst, it can be concluded that $HF\cdot BF_3$ superacid catalysis has considerable potential for commercial application in the bitumen upgrading industry.

ACKNOWLEDGEMENTS

We thank the Alberta Oil Sands Technology and Research Authority for financial assistance.

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