

## THE SIGNIFICANCE OF HYDROGEN DONOR ABILITY AND THE CHARACTERISTICS OF HEAVY OILS/BITUMENS IN COPROCESSING

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### ABSTRACT

The hydrogen donor ability of several heavy oils/bitumens used in CANMET coprocessing and some model compounds was determined using 1,1'-binaphthyl, sulphur and a  $^{13}\text{C}$  NMR technique. Using 1,1'-binaphthyl, it was concluded that generally heavy oils/bitumens are better hydrogen donors than model compounds such as tetralin. When sulphur was used as a hydrogen acceptor, tetralin and hydrogenated anthracene oil showed better hydrogen donor ability than any of the oils used. A good correlation was obtained between coal conversion (THF solubles, Forestburg subbituminous coal) and the per cent of transferable hydrogen determined using sulphur. In addition, the  $^{13}\text{C}$  NMR method, which was carried out on deasphalted heavy oils and bitumens gave slightly higher though similar values of transferable hydrogens.

The effect of "solvent" characteristics on coal and pitch conversions and distillate yields was investigated. Generally coal conversions were not affected by the type of vacuum bottoms used or solvent asphaltene content. Although the amount of indigenous saturated compounds in conventional resids was much higher than those in heavy oils/bitumens, coal dissolutions were equally effective in both types of solvents. Pitch conversions and distillate yields were shown to be more sensitive to the types of resid being processed.

### Introduction

The role and importance of hydrogen donor solvents in coal liquefaction are well known and have been studied by a number of investigators (1-5). It is also known that the hydrogen donor ability of a solvent is not the only criterion that influences the degree of coal solubilization. The physical properties of the solvent also play an important role (6-7). Irrespective of whether physical and chemical properties of solvents play a significant role, the fact is that in all direct liquefaction processes the "quality" of solvent must be maintained during processing if high coal conversion and distillate yields are desired.

In coprocessing, heavy oils/bitumens which can play the role of "solvent" as in coal liquefaction, are also reactants and their roles as hydrogen donors are less understood. In general it is believed that crude derived petroleum resids and bitumens are not as good hydrogen donors compared with solvents such as tetralin, and consequently they are less effective in coal dissolution (8-9). It has been shown by Curtis et al (9) that the addition of good hydrogen donors such as tetralin and 9,10-dihydrophenanthrene in the coprocessing of Maya topped long resid and Illinois No. 6 coal promoted the production of light products.

In spite of the complexity of the chemistry involved in the recycle solvents used in direct coal liquefaction, there is no doubt that the hydrogen donor ability of the solvent is an important factor for the success of any coal liquefaction process. The question of whether the heavy oils/bitumens in coprocessing play a role as significant as that in coal liquefaction in terms of hydrogen donor ability has received little attention.

To address this question we must first understand the basic differences between the two processes. Ideally, in coprocessing there is no recycle solvent and instead fresh solvent is introduced continuously during the process. Unlike an ideal solvent in coal liquefaction, this coprocessing "solvent" is also a reactant and it is upgraded simultaneously with the coal and its chemical composition changes significantly during processing. In CANMET

coprocessing, a mixture of coal and heavy oils/bitumen is processed in a single-stage once-through operation using iron sulphate as a disposable catalyst. Previous results from our laboratory (10) indicated that the *dissolution* of low-rank Canadian coals was relatively insensitive to the type of bitumen or petroleum resid used. However, *resid conversion* depended on the type of resid employed.

The objectives of the present work were: 1) to determine quantitatively the hydrogen donor abilities of different heavy oils/bitumens and conventional crude derived petroleum resids used as oil feedstocks in CANMET coprocessing and attempt to correlate coal dissolution to the amount of transferable hydrogens available in each and 2) to investigate the effect of "solvent" characteristics on coal and pitch conversions.

## Experimental

### *Materials and Feedstocks*

Three crude derived petroleum resids, Boscan, Blend 24 (Venezuela), Maya (Mexico) and Athabasca bitumen and Lloydminster heavy oil vacuum bottoms were obtained from the sample bank of the Primary Upgrading Section, Energy Research Laboratories. IPPL (a vacuum resid from a mixture of sweet crudes from Western Canada) was supplied by the Esso Refinery, Sarnia, Ontario. Cold Lake vacuum bottoms (CLVB) was obtained from the Strathcona refinery of Imperial Oil Ltd, Alberta. Forestburg subbituminous coal from Alberta was supplied by Luscar Limited. Its analysis is shown in Table 1. The 1,1'-binaphthyl from Aldrich was used as received. Raw anthracene oil and hydrogenated anthracene oil were obtained from the Nova Scotia Research Foundation Corporation. The characteristics of the solvents and oils used in this work are shown in Tables 2 and 3.

### *H-donor measurements using 1,1'-Binaphthyl*

For these experiments, the procedure of Kline et al was used (11). The 2-mL reaction vessels were made from 316 SS tubing with end caps. Each sample (0.5 g) was placed in the vessel with 0.5 g 1-1'-binaphthyl and 1.5 g benzene as solvent. The vessels were weighed before the experiment and heated to 430°C for 1 h. A Tecam model IFB 101 fluidized bed sand bath was used as the heating medium. About 2-3 min were required for the reaction vessels to reach the reaction temperature. The vessels were quenched in water, then dried and weighed. Experimental runs having greater than 100 ± 5 wt % material balance were discarded. Each experiment was carried out at least in duplicate.

The contents of the vessels were extracted using THF and analyzed by gas chromatography using a Perkin Elmer Sigma 2000 equipped with 15 m SE-54 capillary column and 3600 data station. The analyses were performed with split mode using an internal standard method. The product analyses were carried out at an initial column temperature of 200°C for 5 min, then temperature programmed at 5°C/minute to 300°C.

### *H-donor measurements using sulphur*

The method used by Aiura et al. for determining transferable hydrogen in coal-derived solvents was modified (H<sub>2</sub>S was quantified by a gas chromatography method rather than by titration) and applied for measuring the donatable hydrogen in bitumens/heavy oils (12). Dehydrogenation experiments using sulphur were performed in a 100 mL stainless steel microreactor at 235±3°C and 1 h residence time. The reactor was charged with 5 g solvent to be tested for donatable hydrogen, 4 g sulphur as hydrogen acceptor and 15 g of phenanthrene as diluent. The reactor was shaken vertically and to aid mixing, two stainless steel balls were placed in the reactor which was pressurized to 100 psig with N<sub>2</sub> at room temperature. After the required residence time the reactor was cooled to room temperature and the gases (H<sub>2</sub>S and N<sub>2</sub>) were collected in a gas bag. The total volume of the gas was measured by water displacement and the composition was determined using a Perkin Elmer Sigma-1B gas chromatograph. From the amount of H<sub>2</sub>S formed, the transferable hydrogen was then determined.

### *Compound type separation and H-donor measurements using $^{13}\text{C}$ NMR*

The amount of transferable hydrogen in four heavy oils/bitumens and conventional resids was also measured using  $^{13}\text{C}$  NMR according to the method described by Aiura et al. (12). The measurements were carried out on the pentane soluble fractions of the materials (asphaltene free). The pentane soluble fractions were separated on a silica column using a Waters 500 preparative chromatograph into saturates (pentane eluted), aromatics (toluene eluted) and polars (methylene chloride and back flash with methyl-tert-butyl ether eluted). The saturated fractions and the original samples (asphaltene free) were subsequently analyzed by  $^{13}\text{C}$  NMR using a Varian XL 300. The amount of transferable hydrogen was calculated from the integrated intensities in the 21-37 ppm range, the carbon contents of the original and the saturated fractions, and the weight per cent of the saturated fractions.

### **Coprocessing experiments**

The coprocessing experiments were carried out in 100 mL stainless steel batch autoclaves equipped with thermowells and pressure transducers. Approximately 20 g of feedstock was placed in the reactor then pressurized with either  $\text{H}_2$  or  $\text{N}_2$  to 800 psig at room temperature. Using a sand bath, about 3 min were required for the reactor to reach the reaction temperature of 420°C. At the end of a run, the reactor was quenched in a water bath. The reactions were carried out either in the presence or absence of iron sulphate catalyst. The iron concentration was kept constant at 0.6 wt % based on maf slurry charged. The volume of the gaseous products was measured and their compositions were analyzed by a gas chromatograph. The slurry products were extracted using pentane, toluene and THF to determine the amount of oils, asphaltenes, and preasphaltenes respectively. Coal conversions were determined from the amount of THF insolubles. Pitch conversions data shown in Table 6 were obtained using a continuous bench scale coprocessing unit.

### **Results and Discussion**

#### *Using 1,1'-binaphthyl as H-acceptor*

The relative hydrogen donor abilities of heavy oils/bitumens and some model compounds measured using 1,1'-binaphthyl are shown in Table 4. At 430°C and in the presence of the hydrogen donors listed in Table 4, 1,1'-binaphthyl is converted to perylene (P) as a major product. Small amounts of rearranged product 2,2'-binaphthyl and a negligible amount of 1,2-binaphthyl were also obtained. The mole ratios of perylene (P) to the sum of 1,1'-binaphthyl plus its rearranged product 2,2'-binaphthyl (B) were taken as measures of the strength of hydrogen donation. The P/B ratios listed in Table 4 are corrected for the amount of perylene formed by heating 1,1'-binaphthyl in the absence of hydrogen donors.

The hydrogen donor abilities for tetralin and 9,10-dihydroanthracene in Table 4 are consistent with those reported by Kline et al (11). The higher values of P/B reported by Kline et al, are attributed to the higher temperature (470°C) employed. For bitumens/heavy oils the P/B ratios remained relatively constant. According to these results using 1,1'-binaphthyl as a hydrogen acceptor, the heavy oils/bitumens tested are better hydrogen donors than tetralin. The mechanism of hydrogen transfer from donor solvents to 1,1'-binaphthyl to form perylene is not well known. It is also unclear why tetralin, which is a good hydrogen donor, does not interact with this reagent as well as heavy oils/bitumens to form perylene. There may be other factors such as physical interactions (favouring heavy oils) that influence the reaction path leading to perylene formation.

In order to correlate the hydrogen donor abilities of bitumens/heavy oils (P/B) for different solvents with coal conversions the dissolution of Forestburg subbituminous coal was studied. In these experiments coal is used as a hydrogen acceptor. Since the objective was to determine the degree of hydrogen transfer from the solvents only to the coal, the experiments were carried out in a nitrogen atmosphere. To prevent coke formation, coal

solubilizations were carried out at a short reaction time of 5 min. The coal conversion results at 5 min in the nitrogen atmosphere and those from 30 min in a hydrogen atmosphere are also shown in Table 4. For comparison, the results of the liquefaction of the same coal in tetralin under similar conditions are given. For the heavy oils/bitumens, coal conversion into THF solubles remained relatively constant. In the nitrogen atmosphere there is a substantial difference in coal conversion between tetralin and the bitumens/heavy oils. In the hydrogen atmosphere the differences are much smaller. As shown in Table 4 it can be concluded that using 1,1'-binaphthyl as a hydrogen acceptor no general correlation can be obtained between P/B and coal conversions for heavy oils/bitumens and model compounds.

#### *Using sulphur as H-acceptor*

Hydrogen donor abilities obtained for heavy oils/bitumens, tetralin, hydrogenated anthracene (HAO) and raw anthracene oils (RAO) using sulphur are shown in Table 5. The amount of transferable hydrogen (TH) for each material was calculated from the amount of H<sub>2</sub>S formed in the reaction of sulphur with these materials. Tetralin and HAO showed the highest amount of TH whereas RAO showed the lowest amount of TH. For the heavy oils/bitumens the weight per cent of TH did not change significantly and remained constant at about 1 wt %.

The coal conversion data both in H<sub>2</sub> (30 min) and N<sub>2</sub> (5 min) atmospheres are also shown in Table 5. Using sulphur as a hydrogen acceptor appears to give a better general correlation between coal conversions and hydrogen donor abilities. The exception to this is between HAO and tetralin where coal conversion (in N<sub>2</sub>) is significantly higher in HAO (lower TH) than in tetralin.

The results indicate that other factors besides hydrogen donor abilities influence coal dissolution. In a hydrogen atmosphere aromatic hydrocarbons present in the solvents with deficient donatable hydrogens become hydrogen shuttlers transferring hydrogen from the gas phase to the free radicals from coal. Since significant amounts of different aromatic structures are present in the heavy oils/bitumens listed in Table 5, relatively high coal conversions are obtained in a hydrogen atmosphere and the difference in coal conversions between any one of these solvents and a relatively good hydrogen donor such as HAO becomes small.

The results also show that although the amount of transferable hydrogen in RAO is considerably lower than the heavy oils/bitumens listed in Table 5, the coal conversion (in N<sub>2</sub>) is similar or higher in this solvent. It can be argued that sulphur may indiscriminately abstract hydrogen from different positions within the molecules of heavy oils/bitumens and that the TH values reported in Table 5 for these materials are not true values for the available hydrogen in hydroaromatic positions. However, as discussed below there is good agreement between dehydrogenation using sulphur and the <sup>13</sup>C NMR methods. Again, other properties of the solvents (like physical properties) may play an important role in coal dissolution besides hydrogen donor ability.

The amount of transferable hydrogen of four heavy oils/bitumens as determined by <sup>13</sup>C NMR is also shown in Table 5. The weight per cent of TH was obtained using the deasphalted fraction of these materials. The <sup>13</sup>C NMR TH values are comparable (within 0.3 for Blend 24 and Athabasca) with the sulphur dehydrogenation method. Irrespective of the method of TH determination, it appears that heavy oils/bitumens having the same amount of TH are capable of dissolving coal to the same degree.

#### *Effect of heavy oil/bitumen characteristics on coal and pitch conversions*

Lett et al (8) in their investigation of the hydrogen donor abilities of heavy oils concluded that heavy oils containing more asphaltenes are better hydrogen donors than those with less asphaltenes. The data presented in Table 5 show that this claim cannot be generalized. Although Athabasca bitumen contains much higher asphaltenes than Blend 24 (Table 3) the amount of transferable hydrogen (measured by <sup>13</sup>C and sulphur dehydrogenation methods) and coal conversions is similar. It has also been pointed out by

Curtis et al (13) that the presence of saturated compounds in liquefaction solvents results in lower coal conversions. The data obtained in our laboratory have shown that in coprocessing, the dissolution of coal is not significantly affected by the amount of saturated compounds present in heavy oils/bitumens. Table 6 shows the compositional characteristics of four heavy oils/bitumens. Although the amount of the saturated fraction is more than twice in Maya compared with Athabasca, the coal conversion did not change significantly (Table 6). However, as was shown earlier by Fouda and Kelly (10), distillate production in coprocessing is sensitive to the type of resid processed. In general, under coprocessing conditions, conventional resids containing higher saturated fractions than bitumens usually produce lower distillate yields and pitch conversions.

### Conclusions

The degree of hydrogen donor ability of heavy oils/bitumens as determined by three different methods was shown to be very similar at least for the heavy oils/bitumens tested. These coprocessing solvents contain approximately 1 wt % transferable hydrogens and are capable of dissolving about 86 wt % coal in a hydrogen atmosphere and about 20 wt % in a nitrogen atmosphere irrespective of their origin. A relatively good correlation was obtained between coal conversion and transferable hydrogens using sulphur as a hydrogen acceptor. The data presented in this paper also show that the weight per cent of saturated fraction and asphaltenes in the heavy oils/bitumens (under CANMET coprocessing conditions) does not influence the degree of coal conversion. It can also be concluded that the hydrogen donor ability of heavy oil/bitumen is not a determining factor in coal solubilization in catalytic coprocessing and definitely is not as significant as in direct coal liquefaction. It is suggested that under a hydrogen atmosphere the aromatic hydrocarbons can act as hydrogen shuttlers transferring hydrogen from the gas phase to coal derived radicals.

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**Table 1 - Analysis of Forestburg coal**Proximate analysis  
(wt %, as received)

Moisture	14.09
Volatile matter	36.37
Fixed carbon	42.67
Ash	6.87

Ultimate analysis  
(wt % daf)

C	71.99
H	4.64
N	1.78
O	20.98
S	0.61

**Table 2 - Elemental Analyses of Oil Feedstocks (wt %)**

Solvents/Oils	C	H	N	O	S
CLVB <sup>a</sup>	82.82	10.57	0.78	0.35	5.66
CLVB(P) <sup>b</sup>	82.62	10.27	0.83	0.26	5.79
Boscan	80.96	10.24	0.90	0.24	5.73
Boscan(P) <sup>b</sup>	81.97	9.83	1.09	0.29	6.40
Maya	84.80	10.10	0.42	< 0.50	4.30
Blend 24 <sup>c</sup>	84.31	10.90	0.81	0.33	3.45
Athabasca	82.30	9.60	0.67	0.69	5.96
IPPL <sup>d</sup>	86.40	10.90	0.43	< 0.50	1.71
Lloydminster	83.20	9.84	0.54	0.61	5.73
Raw anthracene oil	91.50	5.74	1.04	0.56	0.58
Hydrogenated anthracene oil	90.60	9.10	0.15	0.26	0.00

<sup>a</sup> Cold Lake vacuum bottoms, <sup>b</sup> + 525°C fractions, <sup>c</sup> Venezuela blend vacuum bottoms, <sup>d</sup> vacuum bottoms from a blend of Western Canadian crudes (IBP = 560°C)

**Table 3 - Characteristics of Heavy Oil/Bitumen Feedstocks**

Solvents/ Oils	Pentane	Toluene	Pitch <sup>a</sup>	CCR	gravity (°API)	Mn <sup>1</sup>	f <sub>a</sub> <sup>2</sup>
	Inso. (wt %)	Inso. (wt %)	wt %	wt %			
CLVB <sup>b</sup>	23.5	0.20	83.2	17.1	4.82	788	31
Boscan	22.3	0.09	64.6	16.7	7.77	613	30
Maya	22.3	0.11	86.0	18.4	---	756	34
Blend 24 <sup>c</sup>	21.5	<0.10	18.6	6.95	---	848	30
Athabasca	38.4	1.21	99.3	23.9	1.49	983	34
IPPL <sup>d</sup>	14.0	0.92	100.0	15.6	9.86	910	30
Lloydminster	37.4	0.22	90.7	22.0	3.39	1081	35

a +525°C fraction, b Cold Lake vacuum bottoms, c Venezuela blend vacuum bottoms, d vacuum bottoms from a blend of Western Canadian crudes (IBP=560°C),  
<sup>1</sup> number average molecular weight (VPO),  
<sup>2</sup> aromaticity (<sup>13</sup>C NMR)

**Table 4 - Hydrogen donor abilities of model compounds and heavy oils/bitumens measured using 1,1'-binaphthyl and conversion of Forestburg coal**

Material	P/B x 100 <sup>a</sup>		Coal conversion <sup>b</sup>		Coal conversion <sup>c</sup>	
	H <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub>
1,1'-Binaphthyl	0.19	---	---	---	---	---
Tetralin	0.51 (1.3) <sup>4</sup>	91.7	91.7	59.8	---	---
9,10-Dihydroanthracene	10.00 (17.7) <sup>4</sup>	---	---	---	---	---
CLVB <sup>1</sup>	5.50	88.7	88.7	22.1	---	---
CLVB(P) <sup>2</sup>	6.90	---	---	---	---	---
Boscan	5.40	88.3	88.3	20.1	---	---
Boscan(P) <sup>2</sup>	7.20	85.1	85.1	21.3	---	---
Maya	7.00	82.7	82.7	19.1	---	---
Blend 24 <sup>3</sup>	5.70	86.7	86.7	21.9	---	---

<sup>a</sup> moles of perylene to moles of 1,1'-binaphthyl + moles of byproducts  
<sup>b</sup> conversion to THF solubles at 420°C, 30 min and 800 psi H<sub>2</sub>  
<sup>c</sup> conversion to THF solubles at 420°C, 5 min and 800 psi N<sub>2</sub>  
<sup>1</sup> Cold Lake vacuum bottoms, <sup>2</sup> +525°C fractions, <sup>3</sup> Venezuela blend vacuum bottoms  
<sup>4</sup> values taken from reference 11.

Table 5 - Comparison of hydrogen donor abilities of different solvents/oils and coal conversions.

Solvents	Transferable hydrogen (wt %)		Coal conversion (wt %, maf)	
	Sulphur	<sup>13</sup> C NMR	H <sub>2</sub> , 30 min.	N <sub>2</sub> , 5 min
Tetralin	2.01	----	91.7	59.8
CLVBA	1.20	1.28	88.7	22.1
Blend 24 <sup>b</sup>	1.01	1.32	86.5	21.9
Athabasca	1.02	1.30	86.6	20.8
Maya	1.07	1.13	82.7	19.1
Boscan	1.24	----	88.3	20.1
Boscan (P) <sup>c</sup>	1.17	----	85.1	21.3
IPPLD	0.98	----	83.7	19.1
Lloydminster	1.18	----	86.6	20.0
Raw anthracene oil	0.33	----	72.1	26.1
Hydrogenated anthracene oil	1.82	----	94.8	78.2

<sup>a</sup>Cold Lake vacuum bottoms, <sup>b</sup>Venezuela blend vacuum bottoms C +525°C fractions, <sup>c</sup>vacuum bottoms from a blend of Western Canadian crudes (IBP=560°C)

Table 6 - Hydrocarbon type separation of heavy oils/bitumens (wt %): Effect of solvent Characteristics on coal and pitch conversions.

Solvent/oils	Saturates	Aromatics	Polars	Pitch conv. c	
				Coal conv.	Pitch conv. c
CLVBA	28.66	58.68	12.66	88.7	34.1 (68.4)
Athabasca	19.50	65.81	14.68	86.6	40.6 (69.0)
Blend 24 <sup>b</sup>	36.38	51.13	12.49	86.5	36.0 (62.2)
Maya	41.51	50.82	7.68	82.7	----

<sup>a</sup>Cold Lake vacuum bottoms, <sup>b</sup>Venezuela blend vacuum bottoms, <sup>c</sup> results from continuous operation at 425°C and (450°C)