

THE CHEMICAL MODIFICATION OF A BITUMEN
AND ITS NON-FUEL USES

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The development of the Athabasca tar sands has become one of the major advances of the petroleum industry. However, it is evident that the production of materials from the bitumen is only just beginning and with the introduction of gas turbine, electric, propane autos and the like, it is possible that the future of the tar sands lies not in the production of gasoline but in the use of the bitumen as a chemical raw material. In the present communication, we report some simple chemical conversions that may be employed to introduce functional groups into the bitumen* and some preliminary investigations on the uses of the products.

CHEMICAL REACTIONS

As a result of structural studies, it is evident that petroleum asphaltenes are agglomerations of compounds of a particular type (1, 2). Thus, it is not surprising that asphaltenes will undergo a wide range of interactions, of chemical and physical nature, based not only on their condensed aromatic structure but also on the attending alkyl and naphthenic moieties. In the following discussion, we will again rely heavily on the evidence accumulated, for the major part, in our own laboratories, which has either been published elsewhere or is in preparation.

Oxidation

Oxidation of Athabasca asphaltenes with a series of common oxidising agents, i.e., acidic and alkaline peroxide, acidic dichromate, and alkaline permanganate, is a slow process there being < 10% of the product soluble in alkali after treatment with the oxidant for ca. 30 hr. (4). It is evident, however, from the elemental ratios in the products that some oxidation has occurred. Moreover, the occurrence of a broad band centred at 3420 cm^{-1} and a weaker band at 1710 cm^{-1} indicates the formation of phenolic and carboxyl groups on the asphaltene molecules. The H/C ratios of the partially-oxidised products indicate that there are two predominant oxidation routes, notably (i) the oxidation of naphthene moieties to aromatics and active methylene groups to ketones which would reduce the H/C ratios and (ii) more severe oxidation of naphthene and aromatic functions resulting in partial degradation of these systems to carboxylic acid functions whereby the overall effect is diminishing aromatic, but increasing alkane, moieties. Investigation of the partially oxidised materials by proton magnetic resonance spectroscopy (4) provides information about the structural changes which occur during the oxidation processes and an overall picture of these effects is a decrease in size of the condensed aromatic sheet as well as a slight decrease in the degree of substitution of the sheet and a decrease in average chain lengths of the alkyl substituents.

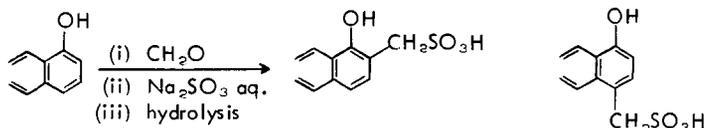
Use of a more severe oxidising agent, i.e. concentrated nitric acid, brings about good conversion of the asphaltenes to water- and alkali-soluble materials (5).

* For convenience, we describe the reactions of the asphaltenes - a fraction considered somewhat useless (except for fuel purposes) by many workers.

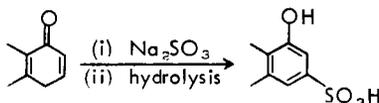
Sulphonation and Sulphomethylation

Sulphomethylation and/or sulphonation of the asphaltenes are not feasible processes because of the lack of functional groups within the asphaltene molecule. Nevertheless, oxidation of the asphaltenes does produce the necessary functional groups and subsequently sulphomethylation and sulphonation can be conveniently achieved (5). Confirmation that sulphomethylation and sulphonation of the oxidized asphaltenes occurs can be obtained from three sources, namely, (i) overall increases in the sulphur contents of the products relative to that of the starting material; (ii) the appearance of a new infrared absorption band at 1030 cm^{-1} attributable to the presence of sulphonic acid group(s) in the molecule(s) (6); and (iii) the water-solubility of the products – a characteristic of this type of material (7, 8). These sulphomethylated and sulphonated oxidized asphaltenes even remain in solution after acidification with 5% aqueous hydrochloric acid to a pH of 2.5–3.0, while the parent oxidized asphaltenes can be precipitated from alkaline solution by acidification to a pH of 6.5.

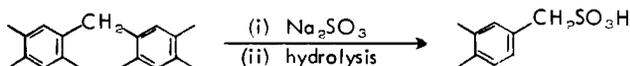
The facile sulphomethylation reaction indicates the presence in the starting materials of reactive sites ortho or para to a phenolic hydroxyl group, e.g.:



while the comparative ease of sulphonation suggests the presence of quinoid structures in the oxidized materials, e.g.:



Alternatively, active methylene groups in the starting materials would facilitate sulphonation by:



since such groups have been known to remain intact after prolonged oxidation (9).

Halogenation

Halogenation of the asphaltenes occurs readily to afford the corresponding halo-derivatives (10) and is accompanied by weight increases in the products. The physical properties of the halogenated materials are markedly different from those of the parent asphaltenes. For example, the unreacted asphaltenes are dark brown, amorphous, and readily soluble in benzene, nitrobenzene, and carbon tetrachloride but the products are black, shiny, and only sparingly soluble, if at all, in these solvents.

There are also several features whereby the individual halogen reactions differ from one another. For example, during chlorination there is a cessation of chlorine uptake by the asphal-

tenes after 4 hours. Analytical data indicate that more than 37% of the total chlorine in the final product is introduced during the first 0.5 hour, reaching the maximum after 4 hours. Furthermore, the H/C ratio of 1.22 in the parent asphaltenes [(H + Cl)/C ratio in the chlorinated materials] remains constant during the first two hours of chlorination, by which time chlorination is 88% complete. This is interpreted as substitution of hydrogen atoms by chlorine in the alkyl moieties of the asphaltenes while the condensed aromatic sheets remain unaltered since substitution of aryl hydrogens only appears to occur readily in the presence of a suitable catalyst, e.g. FeCl_3 , or at elevated temperatures. It is only after more or less complete reaction of the alkyl chains that addition to the aromatic rings occurs as evidenced by the increased (H + Cl)/C ratios in the final stages of chlorination.

Bromine uptake by the asphaltenes is also complete in a comparatively short time (< 8 hr.). However, in contrast to the chlorinated products, the (H + halogen)/C ratio remains fairly constant (1.23 and 1.21 in the bromo-asphaltenes, cf. 1.22 in the unreacted asphaltenes) over the prolonged periods (up to 24 hr.) of the bromination.

Iodination of the asphaltenes is different insofar as a considerable portion of the iodine, recorded initially as iodine uptake, can be removed by extraction with ether or with ethanol whilst very little weight loss is recorded after prolonged maintenance of the material in a high vacuum. The net result is the formation of a product with a (H + I)/C ratio of 1.24 after 8 hr. reaction whilst a more prolonged reaction period affords a product having a (H + I)/C ratio of 1.17. This latter result may be interpreted as iodination of the alkyl or naphthenic moieties of the asphaltenes with subsequent elimination of hydrogen iodide. Alternatively, oxidation of naphthenic moieties to aromatics or oxidative coupling of asphaltene nuclei would also account for lower (H + I)/C ratios. In fact, this latter phenomenon could account, in part, for the insolubility of the products in solvents which are normally excellent for dissolving the unchanged asphaltenes.

Halogenation of the asphaltenes can also be achieved by use of sulphonyl chloride, iodine monochloride, and N-bromosuccinimide or via the Gomberg reaction (11), whereby products similar to those described above are produced.

Attempted water-solubilization of the asphaltenes by treatment of the halo-derivatives with aqueous sodium hydroxide or with aqueous sodium sulphite is not a feasible process (11). Indeed, the hydrolyzed products remained insoluble in strongly alkaline solution. That partial reaction occurs is evident from the decreased (H + Cl)/C ratios and the increased O/C ratios of the products relative to those of the parent halo-asphaltenes. The infrared spectra of the products showed a broad band centered at 3450 cm^{-1} , assigned to the presence of hydroxyl groups in the products, but it was not possible to establish conclusively the presence of sulphonic acid group(s) in the product from the sodium sulphite reaction by assignment of infrared absorption bands to this particular group.

Reactions with Metal Salts

Interactions of asphaltenes with the metal chlorides yield products containing organically-bound chlorine but the analytical data are indicative of dehydrogenation processes occurring simultaneously (12). There is, of course, no clear way by which the extent of the dehydrogenation can be estimated but it may be suggested that it is a dehydrogenation condensation rather than elimination with olefin formation; infrared spectroscopy did not show any bands that could be unequivocally assigned to $\text{C}=\text{C}$ bond vibrations, nor did proton magnetic resonance (p.m.r.) spectroscopy show any olefinic protons. Thus, the mode of dehydrogenation is assumed to involve predominantly inter- or intramolecular condensation reactions insofar as the solubilities and

apparent complexities of the products varied markedly from those of the starting materials and these differences could not be attributed wholly to the incorporation of chlorine atoms into the constituents of the asphaltenes or heavy oil. Indeed, the data accumulated are indicative of a condensation dehydrogenation or, in part, loss of alkyl substituents as, for example, lower molecular weight hydrocarbons during the reactions. As an illustration of the former, the cokes produced during the thermal cracking (450°C) of the asphaltenes or heavy oil have H/C ratios in the range 0.59 - 0.77 (16), while the majority of the insoluble materials produced in the asphaltene/metal chloride reactions have only slightly higher (H + Cl)/C ratios (0.88 - 1.10).

Reactions with Sulphur and Oxygen

Reactions of asphaltenes with sulphur and oxygen have also received some attention and have yielded interesting results (13). For example, treatment of the asphaltenes with oxygen or with sulphur at 150 - 250°C yields a condensed aromatic product [H/C = 0.97, cf. H/C (asphaltene) = 1.20] containing very little additional oxygen or sulphur. The predominant reaction here appears to be condensation between the aromatic and aliphatic moieties of the asphaltenes effected by elemental oxygen and sulphur which are in turn converted to hydrogen sulphide and water. In the former case, i.e. with oxygen, condensation appears to precede in preference to molecular degradation but we note that prolonged reaction times afford lower molecular weight products. Treatment of the condensed products at 200 - 300°C for 1-5 hr. again affords good grade cokes (H/C = 0.54 - 0.56). In all instances the final products contained only very low amounts of elements other than carbon and hydrogen (i.e. Σ NOS < 5% w/w) - a desirable property of good grade coke.

Phosphorylation

Attempts to phosphorylate asphaltenes with phosphoric acid, phosphorous trichloride or phosphorous oxychloride were partially successful insofar as it is possible to introduce up to 3% w/w phosphorous into the asphaltenes (14). However, application of these same reactions to oxidised asphaltenes increases the uptake of phosphorous quite markedly there being up to 10% w/w in the products (14). Subsequent reaction of the phosphorous-containing products are necessary to counteract the acidity, where necessary, of the phosphorous moieties.

Hydrogenation

Montgomery and his co-workers (15, 16) studied the reduction products of tar sand asphaltenes and noted that considerable amounts of hydrogen could be added to the asphaltenes whilst some sulphur was removed. Other studies of the hydrogen processes have been performed mainly with the effects of additional hydrogen on the cracking when increased yields of paraffins were observed (3).

Miscellaneous Chemical Conversions

Other reactions of the asphaltenes have also been performed but the emphasis has mainly been on the formation of more condensed materials to produce good grade cokes. For example, thermal treatment of the halogenated derivatives affords aromatic cokes [H/C = 0.58, cf. coke from the thermal conversion of asphaltene at ~ 460°C has H/C = 0.77] (13, 17) containing less than 1% w/w halogen. Other investigations (13) also show that treatment of the halo-asphaltenes with suitable metal catalysts, e.g. copper at 200 - 300°C/1-5 hr. or sodium at 80 - 110°C/1-5 hr., yield aromatic (H/C = 0.55 - 0.86, respectively) coke-like materials having 0.5 - 3% w/w halogen. Residual halogen may finally be removed by treatment at 300°C for 5 hr. The implications of these investigations to the petroleum industry are many-fold but

perhaps the most significant are (a) the comparatively lower temperatures required for coking due to the presence of bonds in the asphaltenes which are relatively labile and (b) the use of oxygen or sulphur as condensing and aromatising agents without being significantly incorporated into the ensuing coke. Further work on the catalytic effects of other readily available inorganic and organic materials on the coking process are still under investigation and all of the data will be reported in detail in due course.

Other chemical modifications pursued in our laboratories include metallation of the asphaltenes or halo-asphaltenes using metal or metallo-organics followed by, for example, carboxylation to the end product. Interaction of the asphaltenes with *m*-dinitrobenzene affords an oxygen-enriched material which, when treated with hydroxylamine or an amine yields materials containing extra nitrogen. Similarly, reaction of the asphaltenes with maleic anhydride and subsequent hydrolysis yields products bearing carboxylic acid functions.

APPLICATIONS

The traditional uses of petroleum involve the derivation of chemicals from the oil during a refinery operation. It is usual that at some stage during the operation any asphaltenes are removed either as a sludge to be discarded later or to serve as a fuel. In the foregoing discussion we have attempted to show how the asphaltenes may be regarded as chemical entities which are able to undergo a variety of chemical or physical conversions to, perhaps, more useful materials. The overall effects of these modifications is the production of materials which either afford good grade aromatic cokes comparatively easily or the formation of products bearing functional groups which may be employed as a non-fuel material. To date, our main tests have centred around the sulphonated and sulphomethylated materials and their derivatives which have satisfactorily undergone investigations for drilling mud thinners giving results comparable to those obtained with commercial mud thinners (Table 1). In addition, their ability to lower surface tension in aqueous solution indicates that these compounds may also find use as emulsifiers for the *in situ* recovery of the Athabasca bitumen (Table 2) (18). There are also indications that these materials and other similar derivatives of the asphaltenes, especially those containing functions such as carboxylic or hydroxyl will readily exchange cations and could well compete with synthetic zeolites. Other uses of the hydroxyl derivatives and/or the chloro-asphaltenes include high temperature packings or heat transfer media.

The reactions incorporating nitrogen and phosphorus into the asphaltenes are particularly significant at a time when the effects on the environment of many materials containing these elements are receiving considerable attention. Here we have potential slow-release soil conditioners which will only release the nitrogen or phosphorus after considerable weathering or bacteriological action. One may proceed a step further and suggest that the carbonaceous residue remaining after release of the hetero-elements may be a benefit to humus-depleted soils such as the grey-wooded and solonchic soils found in Alberta. It is also feasible that coating a conventional quick-release inorganic fertiliser with a water-soluble or water dispersible derivative will provide a slower-release fertiliser and an organic humus-like residue. In fact, variations of this theme are multiple.

Only further work will tell how practical these projected uses may be and none should be discounted as long as research continues and the need for new uses of petroleum remains.

ACKNOWLEDGMENTS

The authors are indebted to Syncrude Canada Ltd. for gifts of bitumen.

TABLE I
Thinning Properties and Comparison of Water-Soluble Asphaltenes with Commercial Thinners

Designation	lb/bbl	NaOH lb/bbl	CaO lb/bbl	pH	Viscosity 600 rpm	Plastic viscosity centipoise	Yield Point lb/100 sq. in.	--Gel Strength-- 10 sec	10 min
• Base Mud		2	5	12.4	77	7	63	20	32
Sulphomethy- lated asphaltene	2	-	-	11.6	17	5	7	2	3
	4	-	-	11.5	21	6	9	1	4
	6	-	-	11.5	19	7	5	0	4
Sulphonated asphaltenes	2	-	-	11.5	22	10	2	1	2
	4	-	-	11.5	18	8	2	0	1
	6	-	-	11.5	18	8	2	0	1
UNI-CAL	2	-	-	12.6	13	6	1	0	4
	4	-	-	12.6	13	6	1	0	0
	6	-	-	12.6	13	6	1	0	0
SPERCENE	2	-	-	12.6	14	5	4	3	5
	4	-	-	12.6	14	6	2	0	2
	6	-	-	12.6	19	7	5	0	7
PELTEX	2	-	-	12.5	12	5	0	0	0
	4	-	-	12.5	13	6	1	0	0
	6	-	-	12.5	12	5	2	0	2

• Aqueous suspension of 25 lb/bbl Wyoming bentonite, 5.0 lb/bbl lime, and 2.0 lb/bbl sodium hydroxide.

TABLE 2

Surface tensions of ozonised and ozonised-sulphonated bitumen

Concentration % w/w	Surface tension, dynes/cm	
	Ozonised bitumen	Ozonised-sulphonated bitumen
0.1	62	48
0.5	62	41
1.0	52	39

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