

Mesophase Formation in Hydrocarbon Fractions of Bitumen

B.N. Nandi and D.J. Patmore
Energy Research Laboratories, CANMET
Energy, Mines and resources Canada, Ottawa K1A 0G1

D.K. Banerjee and K.J. Laidler
Chemistry Department, University of Ottawa, Canada

Introduction

The tendency for coke formation during the upgrading of Canadian bitumen at elevated temperatures is well known and this phenomenon could lead to some technical difficulties in processing. It is therefore important to gain some insight into the mechanism of coke formation from bitumen. This coke formation process is very complicated as the bitumen is composed of a mixture of many organic and inorganic compounds (1). The proportion of these compounds vary considerably according to the source of the material. An attempt has been made to separate the bitumen into different fractions which are further subjected to physical, chemical and petrographic studies.

The kinetics of coke formation and its relation to the development of mesophase during the pyrolysis of bitumen and its various fractions at different temperatures are the objectives of this study. The kinetic studies have been reported elsewhere (2). Only the development and nature of the mesophase is discussed in this paper.

Experimental

(a) Separation of Fractions

Athabasca bitumen from Alberta, Canada was used for this study. The bitumen was separated into five fractions: asphaltene, soft resin, hard resin, aromatics and saturates.(2)

Asphaltene was separated according to the ASTM method and the maltenes were further separated into hard and soft resins on an activated Altapulvis clay column. Oil was fractionated into aromatics and saturates on an activated alumina-silica column. The relative percentage of the five main fractions are shown in Table 1.

(b) Elemental Analyses

Analyses for carbon, hydrogen, nitrogen, sulphur and oxygen were carried out on all these fractions and the results are given in Table 2.

(c) Development of Mesophase

Pyrolysis of the fractions from the bitumen was performed in a special furnace using a quartz boat suspended in an atmosphere of nitrogen from 390°C to 510°C at various residence times from 3-15 min. About 200 mg of sample was introduced into the furnace at the required temperature and maintained for the required period of time. The pyrolyzed residue was then cooled by a stream of nitrogen and was further extracted with toluene and filtered. The insoluble residue is termed coke in this work. A pellet was made in epoxy resin and was examined microscopically for mesophase formation.

Discussion

The rate constants and the activation energies were calculated from these results. It was found that the rate of coke formation is greater with a higher degree of aromaticity of the feedstock (2).

For asphaltene the rate of coke formation is very rapid and was highest of all the fractions. This fraction possesses the highest aromaticity (H/C 1.18). A microscopic examination of the residue (pyrolyzed at 420°C for 5 min.) shows coalescence of spheres and formation of flow type mosaic structure shown in Fig. 1.

The aromatic fractions separated from the whole bitumen (H/C 1.46) produced coke at a considerably lower rate than that of the asphaltene fractions. After 15 min. of pyrolysis at 450°C, very little carbonized residue was obtained. Spheres and irregular masses of mesophase were observed in the product (Fig. 2).

There are practically no differences in the aromaticities of hard and soft resins. Both resins were heated to 450°C for 5 min. The carbonized residue from the hard resin shows formation of small mesophase spheres and eventually gives a very fine grain coke structure as shown in Fig. 3. Conversely, soft resin under identical conditions of pyrolysis forms isotropic char

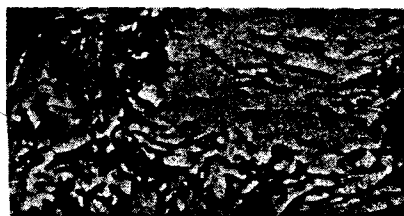


Fig. 1. Coalescence of spheres and flow type mesophase from asphaltene.

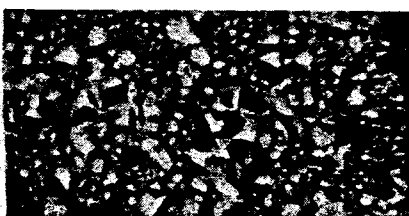


Fig. 2. Spheres and irregular mesophase from aromatics fraction.

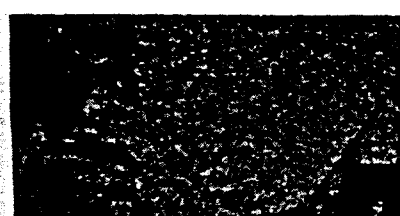


Fig. 3. Fine coke structure from hard resin.



Fig. 4. Isotropic coke from soft resin.

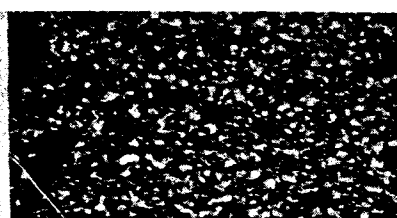


Fig. 5. Coarse grain coke structure from bitumen.

Table 1. Analysis of Athabaska Bitumen.

Asphaltene	18.2
Soft resin	19.2
Hard resin	4.3
Aromatics	36.5
Saturates	21.8

Table 2. Elemental Analysis of the Fractions of Asphaltene.

	C	H	N	O	S	H/C
Bitumen	82.7	10.10	0.48	1.90	4.65	1.46
Asphaltene	79.7	7.9	1.2	1.8	7.9	1.18
Soft resin	79.8	9.7	0.9	3.6	4.7	1.46
Hard resin	78.6	9.8	0.7	4.7	7.8	1.49
Aromatics	89.5	10.9	-	-	-	1.46

Table 3. Coke Yield.

	T °C	Time Min.	%
Asphaltene	420	5	24.0
Soft resin	450	5	20.0
Hard resin	450	5	20.4
Aromatics	450	15	3.6
Saturates	465	5	0.3

as shown in Fig. 4. The microstructure of the pyrolysed whole bitumen is shown in Fig. 5 for comparison.

Conclusions

From the kinetic studies it was observed that the rate of coke or char formation increased with the degree of aromaticity (2).

This is consistent with the microscopic structure of coke (as indicated by the formation of mesophase) from the asphaltene fraction.

The aromaticity of the other three fractions such as aromatics, and soft and hard resins are very close but they form different types of mesophases.

The presence of individual spheres of mesophase from the pyrolysis of the aromatic fraction (Fig. 2) possibly indicates the

presence of saturated side chains or the optimum proportion of aromaticity and aliphaticity as suggested by Ubbelohde (3).

For resin fractions, the hard resin produces very small mesophase spheres whereas the soft resin produces an isotropic char. As these two fractions have similar aromaticities, their behaviour must be related to other differences in chemical compositions.

References

1. Nandi B.N., Belinko K., Ciavaglia L.A. and Purden B.B., Fuel 1978, 57 265.
2. Banerjee D.K., Laidler, K.J. Nandi B.N. and Patmore D.J. "Kinetic studies of Coke Formation in Hydrocarbon Fractions of Heavy Crudes" Communicated to FUEL, Feb. 1985.
3. Ubbelohde A.R., Imperial College, London and personal communication.