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A REVIEW OF SOME CHEMICAL ASPECTS OF THE FORMATION OF COKE DURING THERMAL HYDROCRACKING OF BITUMEN

K. Belinko and J.M. Denis

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A REVIEW OF SOME CHEMICAL ASPECTS OF THE FORMATION
OF COKE DURING THERMAL HYDROCRACKING OF BITUMEN

by

K. Belinko* and J.M. Denis**

ABSTRACT

Reaction mechanisms leading to the formation of coke during thermal hydrocracking of bitumen are discussed. The presence of two structurally different cokes in the thermal hydrocracker is attributed to differences in coking properties of the asphaltenes and the heavy aromatic oils of the bitumen. The chemical structure of the asphaltenes and heavy oils is reviewed with the aim of establishing some relationship between their structure and the type of coke formed when they are carbonized.

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UNE REVUE DE QUELQUES ASPECTS CHIMIQUES DE LA
FORMATION DE COKE PENDANT L'HYDROCRAQUAGE THERMIQUE DU BITUME

par

K. Belinko* et J.M. Denis**

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Dans ce rapport, les auteurs discutent des mécanismes de réaction qui conduisent à la formation de coke pendant l'hydrocraquage thermique du bitume. La présence de deux cokes structurellement différents dans le réacteur thermique est attribuée aux différentes propriétés des asphaltènes et des huiles aromatiques lourdes du bitume. La composition chimique des asphaltènes et des huiles lourdes est revue dans le but d'établir une relation entre leur structure et le genre de coke formé pendant leur carbonisation.

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INTRODUCTION

Thermal hydrocracking has been shown to be a suitable first stage refining process for the Alberta tar sands (1). The technology associated with this method is presently being developed at the Energy Research Laboratories as an integral part of one of CANMET's (Canada Centre for Mineral and Energy Technology) programs. A primary concern associated with the thermal hydrocracking process has been to determine the optimum conditions required to prevent the formation and accumulation of coke in the reactor. Coke formation has been a major cause of fouling during the hydrocracking process (2).

The assumed complexity of coke formation stems primarily from a lack of information on the physico-chemical properties of the various constituents present in bitumen. The subdivision of bitumen into groups such as light oil, heavy oil, resin and asphaltenes has been based predominantly on physical properties, e.g., solubility, molecular weight and boiling point. However, little is known about the chemical structure of most of these constituents. This is particularly true in the case of the higher molecular weight components such as the heavy oils, resins and asphaltenes, for which several conflicting structures have been proposed in the literature (3-8). These higher molecular weight compounds are the most likely precursors for the formation of coke.

It should also be noted that the term "coke" has perhaps been too loosely used to represent the benzene-insoluble residue formed during thermal hydrocracking of bitumen. This has consequently generated some confusion about its physical and chemical nature. In the early part of this century, the term "free-carbon" was used to represent any benzene-insoluble organic residue (9). As time passed, the word "coke" became more popular and is presently used almost exclusively. Although it is true that coke is insoluble in benzene, the inverse is not necessarily true; i.e., benzene-insolubles are not necessarily coke. For example a substantial portion, up to 50%, of the benzene-insoluble residue from the reactor is found to be soluble in quinoline which confirms that the entire residue is not coke (10).

The purpose of this report is to discuss some possible reaction mechanisms leading to the formation of coke. The present state of knowledge relating to the chemical structures of the asphaltenes and other heavy oil fractions will also be reviewed. It was shown in a recent publication that two structurally different cokes form during thermal hydrocracking of Athabasca bitumen (10). This finding was attributed to differences in the coking properties of the asphaltenes and heavy oils. Differences in the chemical structures of the components of the bitumen that may account for the differences in coking properties are also discussed.

GENERAL DISCUSSION

1. Thermal Hydrocracking Process

Thermal hydrocracking of bitumen can be divided into four primary types of reactions:

    (1)   cracking reactions

    (2)   hydrogenation by molecular hydrogen

    (3)   hydrogenation by hydrogen transfer reactions

    (4)   polymerization or condensation reactions

As with most thermal processes, these reactions will either involve or generate free radicals. The stability of these radicals will be determined by the nature of the organic species involved. In general, the most labile radicals will be those that have the least stabilizing properties, and these will include the non-aromatic fractions. Conversely, the most stable radicals will be those that contain extensive unsaturated systems, so that the unpaired electron will be free to spread throughout a large electron volume. Based on similar arguments, hydrogen transfer reactions will generally involve large unsaturated systems as donors and small saturated or slightly unsaturated radicals as acceptors.

In view of the formidable complexity of free radical reactions, it would be very difficult to isolate and identify particular stages of the hydrocracking process. However, it is possible to make some generalizations regarding the various reaction pathways by using some basic chemical princi-

ples. For example, the most reactive species in the reactor will be the highly unstable short chain paraffin radicals formed as a result of thermal cracking:

$$\text{(structure)}{-}CH_2{-}C_2H_5 \longrightarrow \text{(structure)}{-}CH_2^\bullet + C_2H_5^\bullet \qquad [1]$$
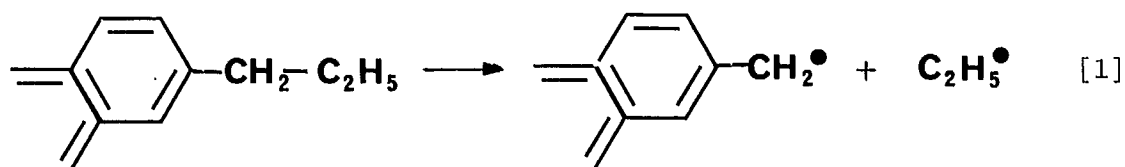
These radicals will seek the most readily available termination pathways. Possible termination pathways are:

(a)   hydrogenation by molecular hydrogen

$$R^\bullet + H_2 \longrightarrow RH + H^\bullet \qquad [2]$$

(b)   reaction with another existing unstable free radical

$$R_1^\bullet + R_2^\bullet \longrightarrow R_1{-}R_2 \qquad [3]$$

$$R_1^\bullet + H^\bullet \longrightarrow R_1H \qquad [4]$$

(c)   hydrogen abstraction (preferably from a large unsaturated system)

$$[5]$$
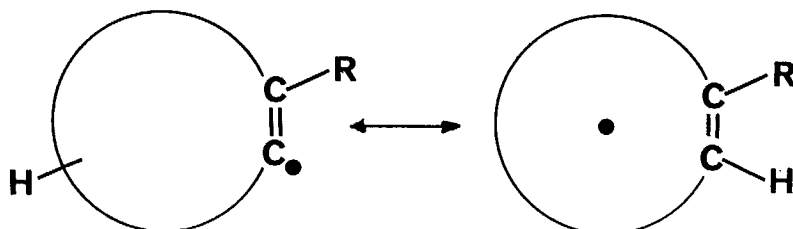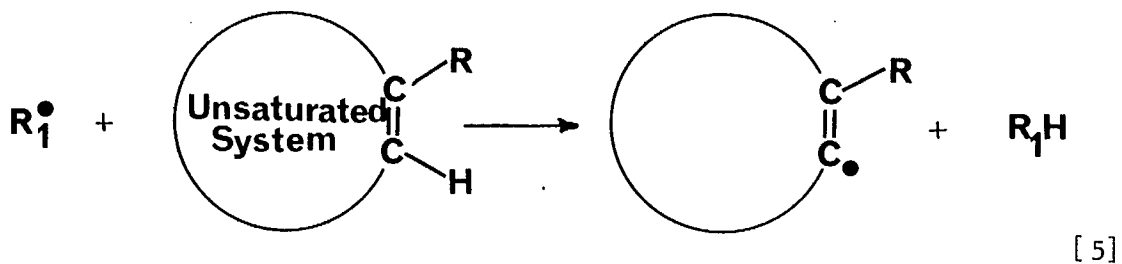
(d)   reaction involving the wall of the reactor

$$R_1^\bullet \; + \; M \longrightarrow R_1^\bullet{-}M \qquad\qquad [6]$$

$$R_2^\bullet \; + \; R_1^\bullet{-}M \longrightarrow M \; + \; R_1{-}R_2 \qquad [7]$$
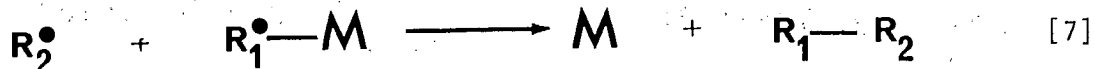
At the other extreme, the least labile radicals, e.g., the large unsaturated systems, will be relatively unreactive towards hydrogenation. Reaction [2] will be energetically unfavourable, especially in the absence of some 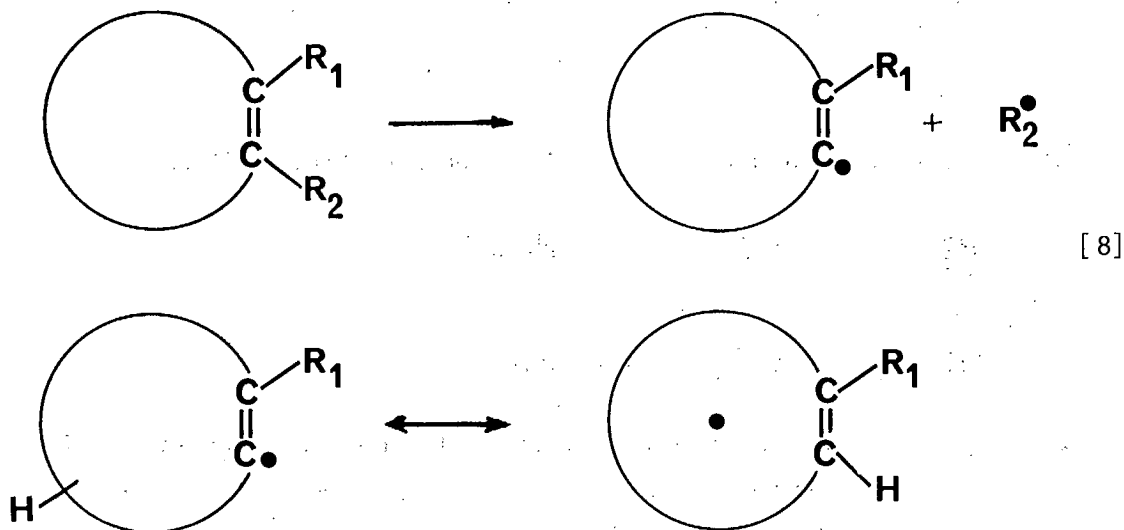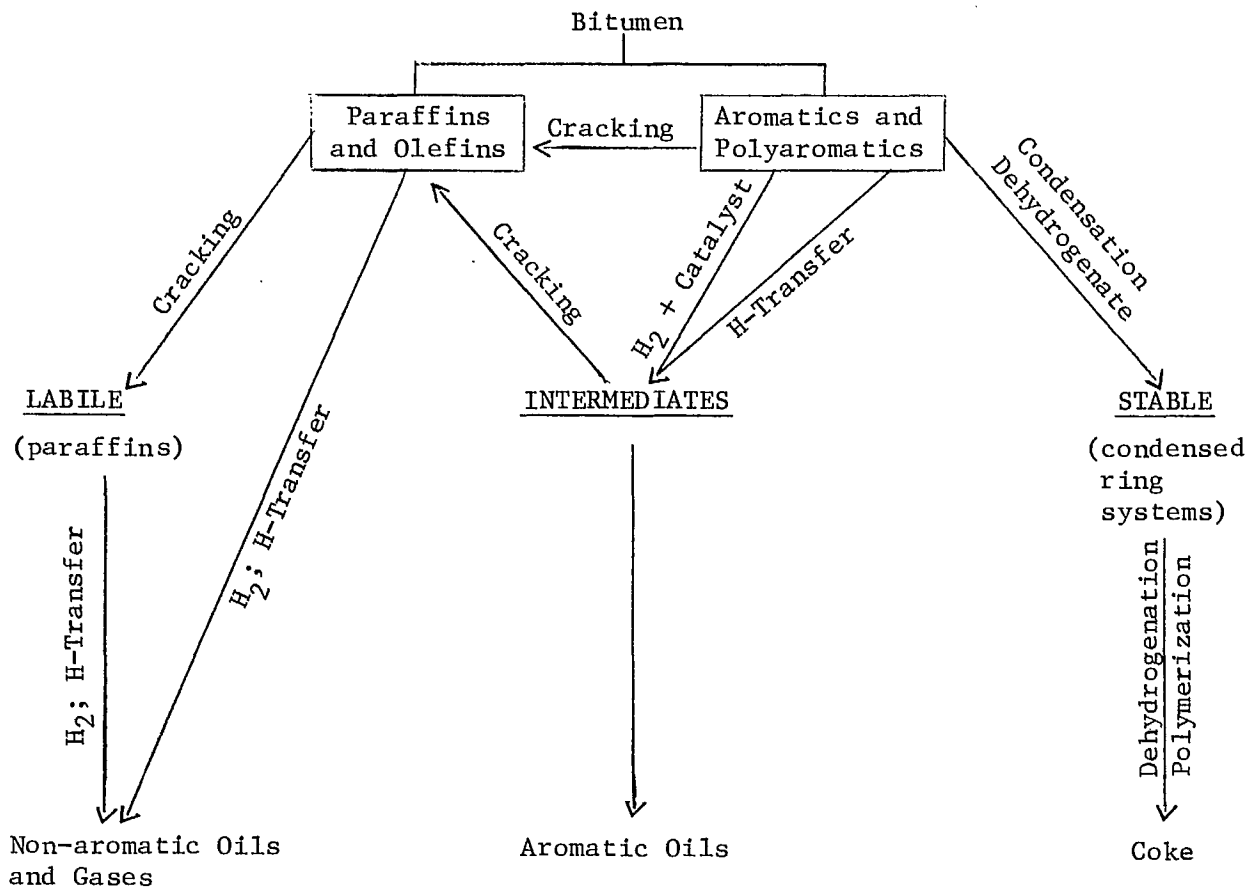catalytic agent. These compounds will undergo extensive cracking of branching chains because of their inherent ability to stabilize radical sites:

[8]

They will also act as excellent hydrogen donors, e.g., reaction [5]. The residual aromatic core of the large unsaturated systems remaining subsequent to the cracking and hydrogen transfer reactions will undoubtedly have extensive radical character, and will therefore seek some form of termination pathway. Since these radicals will be unable to compete efficiently in hydrogenation-type reactions, they will alternatively undergo polymerization reactions, e.g., reactions [6] and [7]. Polymerization and dehydrogenation of these large aromatic radicals will ultimately result in coke formation.

Between these two extremes, compounds will be formed that will be sensitive to prevailing conditions in the reactor. These compounds will probably be competitive towards hydrogenation by molecular hydrogen, especially in the presence of some catalytic agent. Hydrogenation will likely render them more susceptible to further cracking. These compounds will also participate actively as hydrogen acceptors in hydrogen transfer reaction. Upon exhausting all sites for hydrogenation and cracking, the residual aromatic compounds will follow the fate of the larger unsaturated system by participating in the condensation and polymerization reactions which eventually lead to the formation of coke. Residence time in the reactor will consequently be an important parameter in determining the extent of coking of these compounds.

The various processes occurring during thermal hydrocracking of bitumen can be summarized as follows:

Bitumen

| Paraffins and Olefins | Cracking | Aromatics and Polyaromatics |

LABILE (paraffins)   INTERMEDIATES   STABLE (condensed ring systems)

H_2; H-Transfer H_2; H-Transfer   H-Transfer H_2 + Catalyst   Condensation Dehydrogenate   Dehydrogenation Polymerization

Cracking   Cracking

Non-aromatic Oils and Gases   Aromatic Oils   Coke

Based on what has been said, the formation of coke during thermal hydrocracking is an inevitable consequence of the process. Although most of the hydrogenation reactions involve molecular hydrogen, a substantial number rely on hydrogen transfer reactions. The latter result in dehydrogenation of the donor molecules which invariably turn out to be the precursors to coke formation, i.e., the large unsaturated systems. Although formation of coke can not be entirely prevented, it can be minimized by ensuring that there is less dependence on hydrogen transfer reactions in the hydrogenation process. This implies not only that it is crucial to have sufficient molecular hydrogen in the reactor, but also that it is important for the hydrogen to be consumed efficiently. Whereas hydrogenation of the smaller labile molecules by molecular hydrogen is an energetically favoured process, the same is not necessarily true of the larger less labile organic compounds. The latter may require a catalytic agent to aid in the process, and this requirement can perhaps be achieved by the presence of naturally occurring mineral matter in the feed (26,27).

## 2. Chemical Structure of Asphaltenes and Heavy Oils

The polyaromatic compounds in the bitumen which ultimately lead to coke formation are components of the heavy oil fraction, including the resins, and of the asphaltenes. The chemical structure of these polyaromatic compounds has been a topic of extensive controversy in the literature (3-8). Some authors have proposed that these fractions consist of relatively large clusters of condensed aromatic rings (3-5). For instance, based on structural investigations, Speight (5) concluded that the aromatic nuclei of the resins closely resembled dibenzonaphthacene or anthronaphthacene with saturated substituents consisting of 4 to 5 carbon atom units:
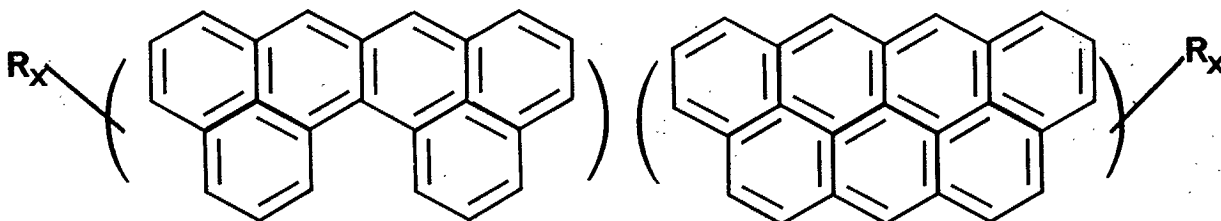
A REVIEW OF SOME CHEMICAL ASPECTS OF THE FORMATION OF COKE DURING
THERMAL HYDROCRACKING OF BITUMEN

This sheet replaces diagrams on pages 6 and 7 of this report.

p. 6 and 7 - The structures for dibenzonaphthacene, anthronaphthacene and
naphtho-ovalene should be given as follows:
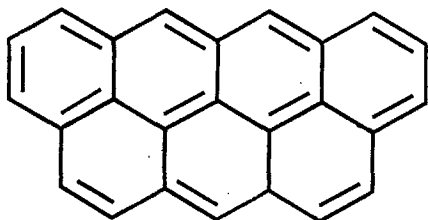
Anthro(defghi)naphthacene
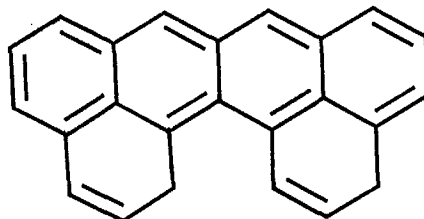
Dibenzo(de,hi)naphthacene

Naphtho(2,7-hijk)ovalene

p. 10 - Reaction [10] should read:

$$\underset{\text{Reduction}}{\longrightarrow} \qquad + \qquad R-CH_2OH$$

The predominant asphaltene structure was found to approximate a naphtho-ovalene structure with more than 50% of the peripheral 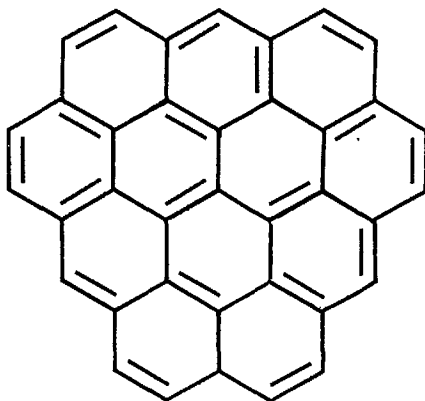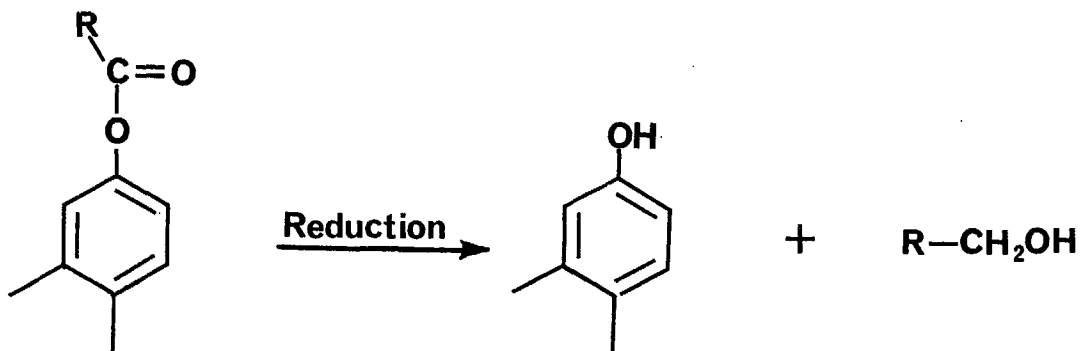hydrogen atoms replaced by alkyl groups. On the basis of molecular weight data, each asphaltene molecule could contain as many as 5 naptho-ovalene nuclei:
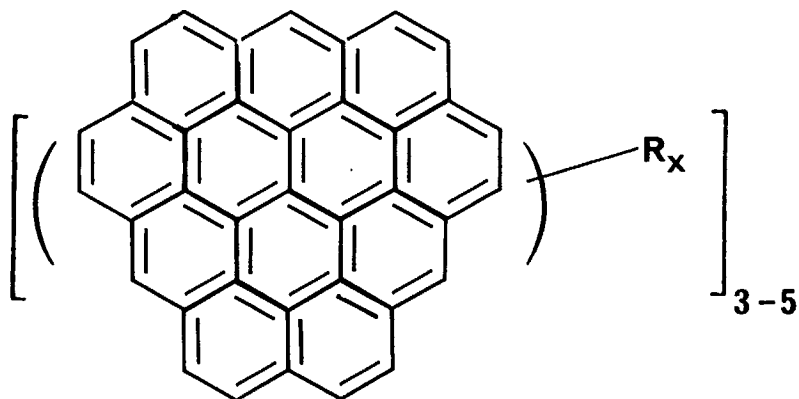
Several authors have argued that the hydrogen-to-carbon ratio of the polyaromatic compounds in the bitumen was too high to be representative of highly condensed polyaromatic structures (6-8). Furthermore, such condensed polyaromatic systems would not be expected to be soluble in benzene and carbon tetrachloride, whereas both the resins and the asphaltenes are quite soluble in these solvents. Therefore, a proposed structure for these compounds has been suggested as follows (6-8):
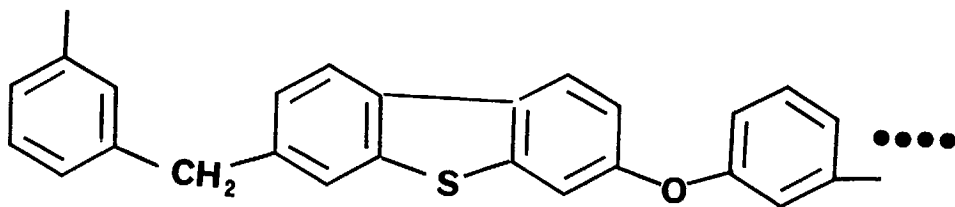
In spite of the varying opinions regarding structure of the polyaromatic components of the bitumen, it has been established that the role of the resins is to provide a transition between the polar asphaltenes and the relatively non-polar oil fractions. The presence of the resins is therefore crucial in preventing the assembly of asphaltene aggregates that otherwise would be insoluble in the bitumen. Various workers (11-13) have demonstrated that although asphaltenes are insoluble in their corresponding oil fraction, dissolution can be brought about by addition of resin. Furthermore, there appears to be an intimate relationship between the asphaltenes and the resins from individual bitumens. While resins from one crude will help dissolve asphaltenes from the same crude, they will not dissolve asphaltenes from a foreign crude (13). The close interrelation between asphaltenes and resins has also been demonstrated by solubility studies. Mitchell and Speight (14) have shown that, while pentane precipitates 17% w/w of the bitumen as asphaltenes, heptane precipitates only 11%, a difference of 35% in the solubility. When asphaltenes previously precipitated from pentane, 'pentane-asphaltenes', were made to dissolve in heptane, only 10% of the 'pentane-asphaltenes' were found to be soluble. However, when resins were added to the 'pentane-asphaltenes' prior to treatment with heptane, 33% of the 'pentane-asphaltenes' were found to be soluble in the heptane.

The function of the resins toward the asphaltenes has been described in terms of a peptizing or protective agent. This enables the asphaltenes to exist in a colloidal configuration within the bitumen. In the absence of sufficient resinous material, flocculation of the asphaltenes occurs within the lyophobic oil fractions of the bitumen.

On the basis of IR-spectroscopy studies, Moschopedis and Speight (15) concluded that the interaction between the resin and the asphaltene molecule involved hydrogen bonding. They found that most of the oxygen in the resins occurred as carbonyl functional groups, primarily as esters (16), while the majority of the oxygen in the asphaltenes appeared as hydroxyl groups, mainly phenolic (17).

The close structural similarities which exist between the asphaltenes and resins have led to suggestions that the asphaltenes are geothermal maturation products of the resins (18,19). Supported by isotopic data, Silverman (19) explained the generation of petroleum by the natural cracking

of a parent source, e.g., lipids. The light hydrocarbons formed by this process would contain more hydrogen than the parent molecule, resulting in dehydrogenation of the latter. Dehydrogenation would be accompanied by polymerization reactions giving rise to the formation of resin and asphaltene molecules. The formation of asphaltene-type molecules from oil and resin fractions has been demonstrated to be experimentally feasible (18,20).

3. Character of the Coke Formed During the Hydrocracking Process

Microscopic examinations of the benzene-insoluble residue collected from the reactor have revealed that two structurally different cokes are formed during the hydrocracking process (10). These cokes were found to originate from the asphaltenes and the heavy oil constituents of the bitumen. The characteristic grain-mosaic type coke derived from the asphaltenes was attributed to the formation of cross-linkage groups during carbonization of this fraction of the bitumen. The absence of extensive cross-linkage groups during carbonization of the heavy oil fraction resulted in a distinctive flow-type coke structure (10). It was generally found that coke from the asphaltenes was far more abundant in the reactor than coke from the heavy aromatic oils. Furthermore, there was evidence to suggest that the asphaltenes underwent precipitation prior to coking (28).

The coke structures derived from the asphaltenes and the heavy aromatic oils substantiated the findings of Moschopedis et al. (16) and Moschopedis and Speight (17) regarding the type of functional groups present in the asphaltene and heavy oil fractions. The phenolic character of the asphaltenes would be expected to give rise to ether groups during carbonization (21-23):

$$2 \text{ } C_6H_5\text{-OH} \quad \xrightarrow{-H_2O} \quad C_6H_5\text{-O-}C_6H_5 \qquad [9]$$
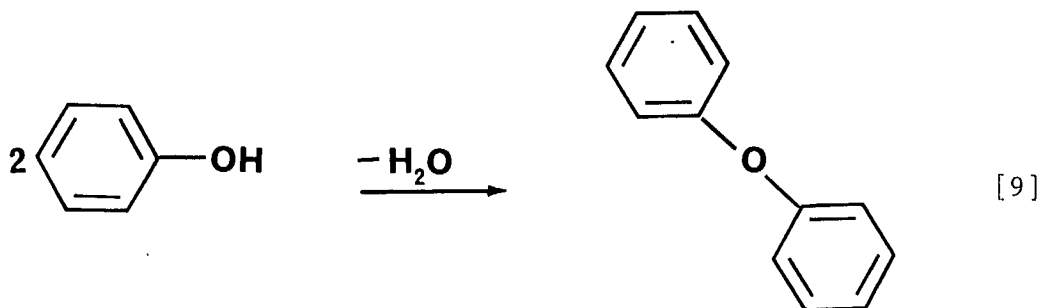
On the other hand, the carbonyl functional groups present in the heavy oils would tend to split off as carbon dioxide or carbon monoxide under hydrocracking conditions. This would generate a free-radical that would be quickly stabilized by reaction with hydrogen before a cross-linkage group could form.

The transformation of the flow-type coke to a grain-mosaic coke from deasphalted heavy oils was possible by two types of pre-treatments (10):

1. reacting the heavy oils with a chemical reducing agent, and
2. addition of elemental sulphur to the deasphalted heavy oil prior to carbonization.

In both cases, the structure of the coke obtained by carbonizing the treated heavy-oils indicated that cross-linkages had been induced during carbonization. Treatment of the deasphalted heavy oils with sulphur gave rise to cross-linkages by sulphur (24,25). Chemical reduction of the heavy oils prior to carbonization may possibly have converted some of the ester functional groups into phenolic groups:
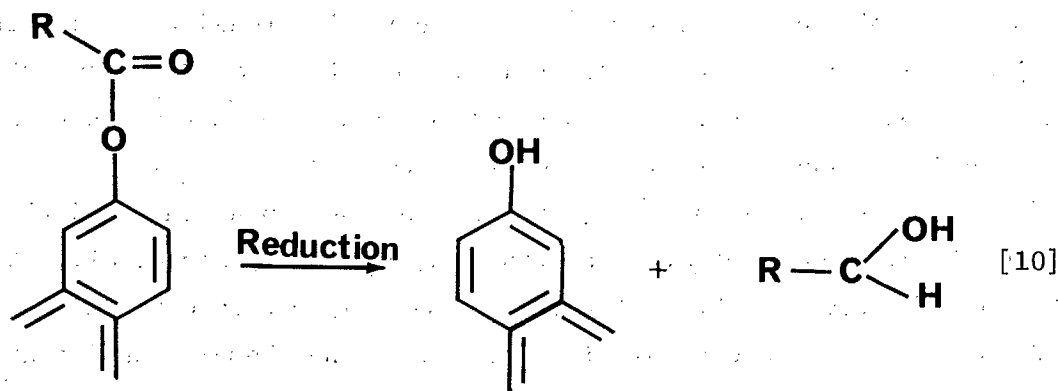
The formation of phenolic groups by reaction [10] would then permit formation of cross-links during carbonization of the reduced deasphalted heavy oils.

CONCLUSIONS

Coke formation during thermal hydrocracking of bitumen results from condensation and dehydrogenation of the large unsaturated systems that are present in the bitumen. These unsaturated systems are primarily the asphaltenes and the heavy aromatic oils. Although there is some controversy regarding the molecular structure of these fractions, it is generally recognized that the solubility of the asphaltenes in the bitumen relies on the presence of the resins, a component of the heavy oils. These resins act as peptizing agents, and consequently prevent flocculation of the asphaltenes. During thermal hydrocracking, the resins would likely lose their protective properties towards the asphaltenes, resulting in precipitation of the latter. The precipitated asphaltenes would then tend to become more susceptible to coking than would any other constituent of the bitumen.

The chemical structure of the asphaltenes and of the heavy aromatic oils appears to be sufficiently dissimilar as to result in differences in their coking properties. The grain-mosaic structure of the asphaltene-coke can be distinguished from the flow-type structure of the heavy oil-coke, and arises primarily from the phenolic character of the asphaltenes. These differences, therefore, provide a means of identifying the coking substance at various stages of the thermal hydrocracking process.

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77-5   Pit slope manual - Chapter 5 - Design; D.F. Coates; Cat. No. M38-14/5-1977, ISBN 0-660-00962-5; Price: $4.25 Canada, $5.10 other countries.

77-6   Pit slope manual - Supplement 5-3 - Financial computer programs; Y.C. Kim, W.C. Cassun and T.E. Hall; Cat. No. M38-14/5-1977-3, ISBN 0-660-00983-8; Price: $4.25 Canada, $5.10 other countries.

77-7   Zinc-copper ore RU-1: Its characterization and preparation for use as a certified reference material; G.H. Faye, W.J. Bowman and R. Sutarno; Cat. No. M38-13/77-7, ISBN 0-660-00896-3; Price: $1.00 Canada, $1.20 other countries.

77-17   Pit slope manual - Supplement 5-2 - Rotational shear sliding: Analyses and computer programs; R. Sage, N. Toews, Y. Yu and D.F. Coates; Cat. No. M38-14/5-1977-2, ISBN 0-660-01009-7; Price: $3.00 Canada, $3.60 other countries.