

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/44093752>

Effect of Thermal and Hydro-Catalytic Treatment on the Molecular Chemistry of Narrow Fractions of Athabasca Bitumen Pitch

ARTICLE *in* ENERGY & FUELS · JANUARY 2001

Impact Factor: 2.79 · DOI: 10.1021/ef0001538

CITATIONS

11

READS

14

5 AUTHORS, INCLUDING:



Suoqi Zhao

China University of Petroleum

95 PUBLICATIONS 1,077 CITATIONS

SEE PROFILE



Keng H. Chung

Well Resources Inc.

117 PUBLICATIONS 1,469 CITATIONS

SEE PROFILE

NRC Publications Archive (NPArc) Archives des publications du CNRC (NPArc)

Effect of thermal and hydro-catalytic treatment on the molecular chemistry of narrow fractions of Athabasca bitumen pitch

Zhao, S.; Kotlyar, L. S.; Woods, John; Sparks, B. D.; Chung, K. H.

Publisher's version / la version de l'éditeur:
Energy & Fuels, 15, 2001

Web page / page Web

<http://dx.doi.org/10.1021/ef0001538>

<http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/ctrl?action=rtdoc&an=14225967&lang=en>

<http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/ctrl?action=rtdoc&an=14225967&lang=fr>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/jsp/nparc_cp.jsp?lang=en

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/jsp/nparc_cp.jsp?lang=fr

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Contact us / Contactez nous: nparc.cisti@nrc-cnrc.gc.ca.

Effect of Thermal and Hydro-Catalytic Treatment on the Molecular Chemistry of Narrow Fractions of Athabasca Bitumen Pitch

S. Zhao

State Key Laboratory of Heavy Oil Processing, University of Petroleum, Beijing, China

L. S. Kotlyar,* J. R. Woods, and B. D. Sparks

National Research Council of Canada, Institute for Chemical Process and Environmental Technology, Montreal Road Campus, Ottawa, Ontario, Canada, K1A 0R6

K. H. Chung

Syncrude Canada Ltd. Edmonton Research Center 9421–17th Avenue, Edmonton, Alberta, Canada, T6N 1H4

Received July 11, 2000. Revised Manuscript Received September 29, 2000

As much as 50 w/w % of bitumen derived from Athabasca oil sands consists of a residuum that cannot be easily upgraded. A better understanding of the chemistry of this material is the key to achieving optimal yields of commercially useful products. In recent years, the application of supercritical fluid extraction (SCFE) with pentane has been successful in separating the residuum into a number of narrow fractions based on their solubility parameters. An important corollary to this separation is that the molecular weight of each fraction increases with the severity of conditions needed to extract the progressively heavier components in each residua. In combination with advanced characterization techniques this approach has proved to be useful in elucidating the complexity of bitumen chemistry. For the work described here, this approach has been applied to residua from commercial operations at the Syncrude Canada Ltd. plant in Northern Alberta. Base samples included virgin bitumen pitch (P) together with residua from the catalytic hydro-cracking (HC) unit and a once-through fluid-coking (CK) test. The SCFE insoluble, heavy sub-fractions in the pitch contain “core” structures, comprising condensed polyaromatic rings, associated with heteroatoms and trace metals. In the catalytic hydro-cracking process the cleavage of C–S side chains and the breakage of inter-unit bonds are the prevailing reactions. A comparison between the lighter, SCFE-soluble fractions from catalytic hydro-cracking and thermal cracking shows the latter to have lower unit molecular weights, higher sulfide contents, and shorter alkyl substituents. The highly aromatic, SCFE-insoluble molecules from the CK process are likely formed from condensation reactions involving various fragments of toluene-soluble and -insoluble material. Condensation reactions between heavy “core” molecules from the SCFE insolubles in pitch lead to formation of coke. In the catalytic hydro-cracking process single unit, highly aromatic, polar “cores” from pitch SCFE insolubles appear to remain toluene-soluble and thus constitute most of the HC residue. These coke precursors will be converted to coke, or pseudo-solid species, if subjected to the thermal treatment applied in coking or severe hydro-cracking.

Introduction

Bitumen derived from Athabasca oil sands is known to exhibit some unique characteristics during conventional refinery processes. As much as 50 w/w % of the bitumen consists of residuum that cannot be easily upgraded. The key to achieving optimal yield and quality of commercially useful products is a better understanding of the molecular chemistry of this residuum. As a step in this direction, the research reported here attempts to define the implications of feedstock molecular chemistry during bitumen upgrading by conventional processes.^{1–4}

The approach adopted is based on the application of supercritical fluid extraction (SCFE) to separate bitumen pitch, or process residua, into multiple fractions with progressively higher molecular weight and complexity. Understanding the chemical nature of these narrow fractions is expected to provide information to allow fine-tuning of existing bitumen upgrading approaches or development of new processes.

- (1) Chung, K. H.; Xu, C.; Hu, Y.; Wang, R. *Oil Gas J.* January, **1997**.
- (2) Chung, K. H.; Xu, C.; Gray, M.; Zhao, Y.; Kotlyar, L. S.; Sparks, B. D. *Rev. Process Chem. Eng.* **1998**, *1*, 41.
- (3) Chung, K. H.; Xu, C. *Fuel* **2000**, in print.
- (4) Zhao, S.; Kotlyar, L. S.; Woods, J. R.; Sparks, B. D.; Chung, K. H. *Pet. Sci. Technol.* **2000**, *18*, 587.

* Author to whom correspondence should be addressed

In our previous communication, we presented the detailed characterization of SCFE fractions from a virgin bitumen pitch.¹⁻⁴ Here we extend that work to SCFE extracts separated from a residuum produced from a commercial catalytic hydro-cracking unit and a once-through fluid-coking test with bitumen pitch. Our results are discussed in terms of the role of molecular chemistry in the refining process.

Experimental Section

Samples. Syncrude Research Ltd. provided three residua, vacuum distilled at 524 °C, from commercial operations: (1) Athabasca virgin bitumen pitch from the hot water extraction process (P); (2) a pitch sample from a once-through fluid-coking (CK) test; and (3) a pitch sample from a catalytic hydro-cracking (HC) test on bitumen. Details on the background of these samples are provided elsewhere.³ The residua were subjected to supercritical fluid extraction with pentane under increasingly severe conditions of temperature and pressure.^{1,2} In each case a significant amount of residual material, or end-cut, was nonextractable under even the most severe conditions. Syncrude Research also provided samples of supercritical pentane-soluble front-cut fractions from the P, CK, and HC samples, together with the corresponding insoluble end-cuts, P-EC, CK-EC, and HC-EC. The end-cut yields were 40.4 w/w %, 17.3 w/w % and 31.8 w/w %, respectively.

Prior to analysis, any solids associated with the samples (BS), mostly inorganic mineral-based material originally present in the bitumen feed, were quantitatively separated from the end-cuts by a procedure described elsewhere.⁵

Further fractionation of the P-EC was achieved on the basis of solubility in different solvent blends.^{4,6,7} Solids-free, desolventized samples were redissolved in toluene, 4:1 by weight and then mixed with an excess of a toluene/pentane blend with molar ratio of 0.47. Precipitated solids (P-EC-1) were separated on a 0.45 μm filter. This procedure was repeated with the soluble fraction from the first treatment using another blend having a molar ratio of 0.25. This produced a second precipitate (P-EC-2) that was again removed by filtration; both of the precipitates were desolventized to produce dry solids. Further, the twice-treated, residual solution was desolventized to produce a third, dry solid fraction (P-EC-3); in increasing order of sample number the three fractions represented 35 w/w %, 19 w/w %, and 46 w/w %, respectively, of the original P-EC sample. Fractionation of asphaltenes by this technique produces different amounts of precipitate depending on the solubility parameter of the solvent blend used.⁷ On the basis of solubility considerations, it is to be expected that progressively more complex, higher molecular weight molecules will be precipitated as the solubility parameter of the blend increases, i.e., with larger amounts of toluene in this case. This was the situation in this work where fraction P-EC-1 was structurally the worst in terms of potential upgradability.

Analyses. Carbon, hydrogen, nitrogen, and sulfur contents were measured using a LECO CHNS-932 analyzer. Oxygen was determined using a LECO VTF-900 attachment. Metals were analyzed by the induced coupled plasma (ICP) method. Gel permeation chromatography (GPC) was used to measure weight (M_w) and number average (M_n) molecular weights for each sample. The method employed tetrahydrofuran as solvent at 40 °C, sample volumes of 0.1 mL at a loading of 0.5 w/v % and polystyrene standards in the range of 900 to 98000. Vapor pressure osmometry (VPO) measurements were carried out on some of the same samples for comparison purposes. In these

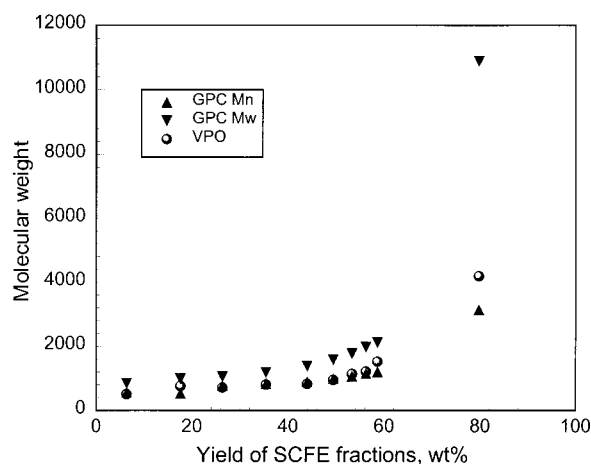


Figure 1. Comparison of VPO and GPC molecular weights for SCFE fractions from bitumen pitch: number average (M_n) and weight average (M_w).

cases benzene was used as the solvent, operating temperature was 45 °C, and determinations were made over a concentration range of 0.3 to 1 w/w %.

A comparison of data for the same samples by the two methods is shown in Figure 1. The yield results in this and subsequent figures are presented to show the average property for each fraction, thereby allowing relative comparisons between SCFE fractions from different sample families. GPC number average molecular weight was selected for use in the estimation of molecular structures in this work based on its similarity with VPO data and ease of operation.

X-ray photo-electron spectroscopy (XPS) spectra for the different solid fractions were recorded using a PHI 5500 Instrument (PHI Electronics, Eden Prairie, Minnesota) with an aluminum K α source of X-rays.

Proton NMR measurements were made with a Varian Unity Inova 400 MHz spectrometer, fitted with a 5 mm, 4-nucleus probe. Each sample (0.1 g) was dissolved in deuterated chloroform (1.0 mL) and placed in a 5 mL NMR tube; this relatively large sample concentration was necessary to obtain a satisfactory signal-to-noise ratio for measurements on these complex molecules. A solution of tetramethylsilane in chloroform (15 μL per 100 g) was used as a reference. Spectra were acquired at a sweep width of 6000 Hz, or 15 ppm, a pulse flip angle of 75°, and a pulse width of 14.8. Pulse repetition time was 15 s with an acquisition time of 5 s and a relaxation delay of 10 s. The 128 transients were collected at an exact frequency of 399.961 Hz. The same spectrometer, with a 10 mm Broad-band Probe, was also used for ^{13}C NMR measurements at a sweep-width setting of 25000 Hz. Each sample (0.35 g) was dissolved in deuterated chloroform (3.5 mL), containing 10 w/w % (0.0286 M) CrAcAc as a paramagnetic relaxation agent. Tetramethylsilane in chloroform (15 μL /100 g) provided a reference. A pulse flip angle of 75° was used along with a pulse width of 8.5. The pulse repetition time was 20 s, with an acquisition time of 5 s and a relaxation delay of 15 s; the number of transients required was 3072. A line-broadening factor of 2 was used for all spectra. Acquisition was performed at an exact frequency of 100.569 Hz.

FTIR spectra were recorded with a Midac FTIR model M1200-SP3 with a cell path length of 0.1 mm. The samples were dissolved in CCl_4 at a concentration of about 50 g/L. The resolution of the spectra was set to 2 cm^{-1} ; 50 scans for each sample were generated in the range 4000–850 cm^{-1} . The methyl and methylene group concentrations were determined on the basis of the areas under the $-\text{CH}_3$ and $-\text{CH}_2$ anti-symmetric vibration absorption bands at 2955 cm^{-1} and 2926 cm^{-1} , respectively.

(5) Kotlyar, L. S.; Sparks, B. D.; Woods, J.; Raymond, S.; Le Page, Y.; Shelfantook, W. *Pet. Sci. Technol.* **1998**, *16*, 1.

(6) Zhao, S.; Kotlyar, L. S.; Woods, J. R.; Sparks, B. D.; Hardacre, K.; Chung, K. H. *Fuel* **2000**, in print.

(7) Mitchell, D. L.; Speight, J. G. *Fuel* **1973**, *52*, 149.

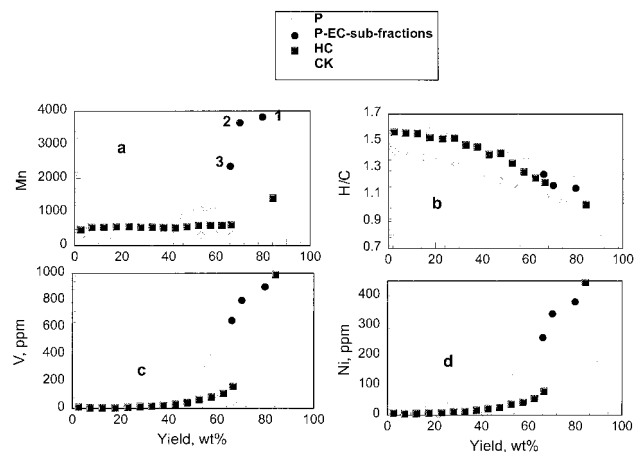


Figure 2. Properties of SCFE fractions from P, HC, and CK: (a) M_n , (b) H/C atomic ratios, and (c) vanadium and (d) nickel contents.

Results

Molecular Weight. Figure 2a presents a side-by-side comparison of the M_n versus average weight percentage yield for the SCFE fractions from the P, HC, and CK samples. Results for P-EC sub-fractions 1, 2, and 3 are also included. For the SCFE front-cuts from pitch, M_n initially increases steadily, followed by a sudden increase for the P-EC sub-fractions. P-EC sub-fraction 1 is the heaviest portion of the pitch with M_n approaching 4000. The M_n of the SCFE extracts from both the HC and CK residua are lower than those for the corresponding fractions from the original pitch. The reduction in M_n for both thermal and catalytically hydro cracked residues is especially prominent in the end-cut samples. On the other hand, the front-cuts of both the HC and CK have a relatively constant M_n with HC molecules being slightly larger than those comprising the CK fractions.

Elemental Analysis. Figure 2b shows that the H/C atomic ratio for all three series decreases with yield. For the front-cuts, the H/C values are similar for the HC and P samples, while those for the CK fractions are lower. The H/C ratios determined for P-EC and its sub-fractions are all much greater than those measured for HC-EC and especially CK-EC.

The vanadium and nickel concentrations in the HC and CK front-cuts are lower than those in the corresponding P samples; see Figure 2c,d. This suggests that hydro-cracking processes are not necessarily more effective for de-metalization than thermal cracking methods.^{8,9} The Ni and V contents of the HC-EC and P-EC-1 samples are similar. The lower metal contents for CK-EC relative to HC-EC may result from disposition of Ni- and V-rich components as coke.¹⁰

For all three series of SCFE fractions there is a gradual increase in nitrogen contents with average yield, see Figure 3a. For the combined front-cuts, representing up to 60% of the total residua, the nitrogen contents for both the HC and CK series are higher than

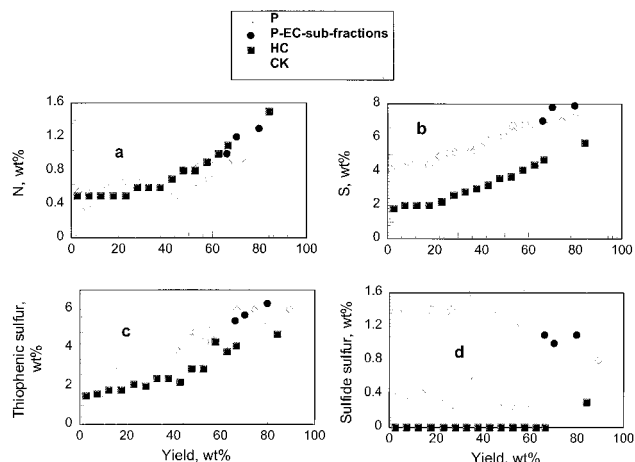


Figure 3. Elemental analysis of SCFE fractions: (a) nitrogen, (b) total sulfur, (c) thiophenic, and (d) sulfide sulfur contents.

those for the corresponding P fractions. Only minor differences between the corresponding front-cuts of HC and CK were observed. At higher yields, the nitrogen content for both P and HC samples increases rapidly whereas changes in the CK fractions are less pronounced. The nitrogen content of the HC-EC is close to that of the heaviest P-EC sub-fraction (P-EC-1). The relatively low nitrogen content of the CK-EC material reflects the disposition of nitrogen rich P-EC sub-fractions in the coke fraction during upgrading.¹⁰

Figure 3b shows an increase in sulfur concentration with yield for all three series. Except for their end-cuts, the sulfur concentrations in the CK and P fractions are essentially the same. For all HC fractions a significant reduction in sulfur concentration has occurred. Earlier work by the present authors demonstrated that XPS is a useful tool for the quantitative evaluation of sulfur types present in Athabasca asphaltene.¹¹ In this research, the method identified thiophenic and sulfide/mercaptide as the two major types of sulfur present in the samples analyzed; others have reported similar findings.¹² For all three series the thiophenic sulfur content increases significantly with average yield, see Figure 3c. As shown in Figure 3d the sulfide/mercaptide contents of the residua do not change much between fractions. Samples from the P resid fractions have the highest sulfide contents, whereas, with the exception of its end-cut, the HC series contains no detectable sulfide. In this respect, hydro-cracking is a more effective desulfurization process than thermal cracking.^{8,9}

Molecular Parameters. Average structural parameters of the various fractions were calculated on the basis of the results of proton NMR, elemental analysis, and M_n .^{6,13,14} These parameters are identified in Table 1 and include the values for the parameter "m", determined from the results of ¹³C NMR. This parameter is related to the number of internal $-\text{CH}_2$ groups per unit in linear alkane substituents ($\text{CH}_3\text{CH}_2-(\text{CH}_2)_m-\text{CH}_2\text{CH}_3$).¹⁵ The degree of branching for ali-

(8) Mosby, J. F.; Butte, R. D.; Cox, J. A.; Nickolaides, C. *Chem. Eng. Sci.* **1986**, *41*, 1148.

(9) Heck, R. H.; DiGuiseppi, F. T. *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.* **1993**, *38*, 417.

(10) Green, J. B.; Sturm, G. P.; Shay, J. Y.; Green, J. A.; Reynolds, J. W.; Young, L. L.; Thomson, J. S. *ACS Div. Pet. Chem.* **1992**, *37* (3), 956.

(11) Zhao, S.; Kotlyar, L. S.; Woods, J. R.; Sparks, B. D.; Chung, K. H. *Energy Fuels*, submitted for publication.

(12) Payzant, J. D.; McIntyre, D. D.; Mojelsky, T. W.; Torres, M.; Montgomery, D. S.; Strausz, O. P. *Org. Geochem.* **1989**, *14* (4), 461.

(13) Brown, J. K.; Ladner, W. R. *Fuel* **1960**, *39*, 87.

(14) Haley, G. A. *Anal. Chem.* **1972**, *43* (3), 371; *ibid.*, **1972**, *44* (3), 580.

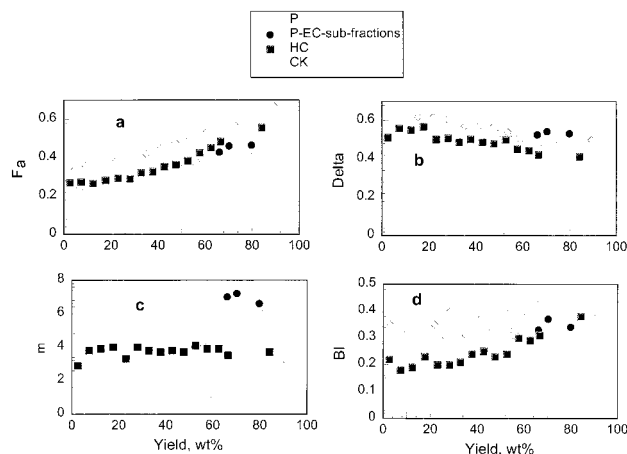


Figure 4. Average structural parameters of SCFE fractions: (a) aromaticity, f_a , (b) degree of aromatic rings substitution (delta, δ), (c) the number of internal $-\text{CH}_2$ groups, m , in long aliphatic chain, and (d) branching index (BI).

Table 1. Structural Parameter Identification

structural parameters	identification
f_a	fraction of total carbon in an aromatic environment (aromaticity)
H_{au}/C_A	atomic hydrogen/carbon ratio of hypothetical unsubstituted aromatic structure
δ	ratio of substituted carbons to peripheral aromatic carbons
n	number of units per molecule
UMW	unit molecular weight
C_α	number of carbons per unit in α position to aromatic rings
C_{AP}	number of peripheral aromatic carbon atoms per unit
C_i	number of internal aromatic carbons per unit
C_f	number of fused aromatic carbons per unit
R_a	number of aromatic rings per unit
R_N	number of naphthenic rings per unit
m	number of methylene groups per unit in straight side chain at least 4 carbons from the chain end and 3 carbons from an aromatic ring ($\text{CH}_3-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_m-\text{CH}_2(\beta)-\text{CH}_2(\alpha)-$); estimated from $\text{C}_{29,7}$ ^{13}C NMR ¹⁵
BI	degree of branching (branching index) of aliphatic substituents; estimated from FTIR results in conjunction with the results of elemental analysis and proton NMR ⁶

phatic substituents, index BI, was calculated from a combination of FTIR data, elemental analysis, and ^1H NMR.⁶

Figure 4a compares the aromaticity f_a values for the various samples calculated from proton NMR data. A smooth increase in f_a with yield is a common trend for each series. All of the CK fractions are more aromatic than the corresponding fractions from the HC, and especially P, series. The calculated aromaticities are similar to the independent values determined directly from ^{13}C NMR and provide a good reliability check. There is a trend for degree of aromatic ring substitution (delta, δ) to decrease with yield for all three series, see Figure 4b. In addition, the δ values for the fractions from the HC samples are lower than those for the other two series. The front-cuts from each series have relatively constant aliphatic chain lengths (m), Figure 4c.

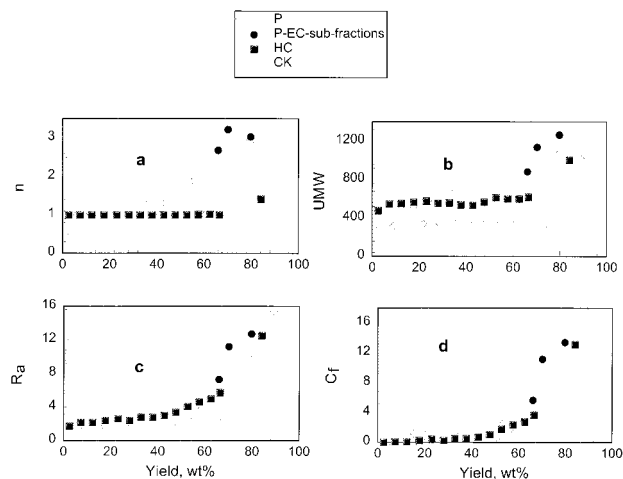


Figure 5. Molecular parameters: (a) number of units, n , (b) unit molecular weight, UMW, (c) number of aromatic rings, R_a , per unit, and (d) number of fused aromatic carbon, C_f , per unit, versus SCFE fractions yield.

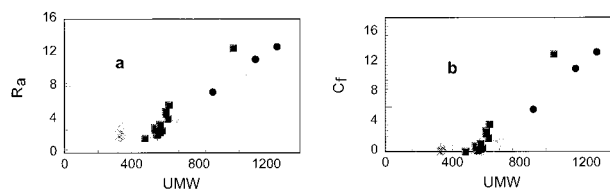


Figure 6. Molecular parameters: (a) number of aromatic rings, R_a , per unit and (b) number of fused aromatic carbon, C_f , per unit, versus UMW of fractions.

For samples CK-EC and P-EC, the m values are greater than those for their corresponding front-cuts. Coking (CK) is more effective at shortening side chains than hydro-cracking (HC). The degree of side-chain branching (BI) increases with average yield in all cases, see Figure 4d. Compared to the P series, the BI values for the CK front-cut fractions are higher while the corresponding results for the same HC fractions are lower. The end-cuts for each series have similar values.

Figure 5, parts a and b, compare the number of repeating units in each molecule (n) and unit molecular weight (UMW). For the front-end P samples, n increases with yield from 1 to 2.2; each molecule in sample P-EC and its sub-fractions contain 2.5 to 3.2 units. With the exception of sample HC-EC ($n = 1.4$) the fractions from both CK and HC are represented by single unit molecules. Figure 5b shows that UMWs for the end-cuts from both thermal (CK) and hydro-cracked (HC) residua are close to those of the original pitch and its sub-fractions. While the front-cut portions of all three series have a relatively constant UMW the CK units are significantly smaller than those comprising the HC and P samples.

The number of aromatic rings (R_a) and fused aromatic carbons (C_f) per unit versus yield of SCFE fractions are shown in Figure 5c,d; the same data is re-plotted against UMW in Figure 6a,b. The values for both R_a and C_f increase with yield. For the front fractions from the P and HC samples, the UMWs all fall within the range of 500–700 and the unit structural parameters, R_a and C_f , are similar. By comparison, the corresponding CK fractions have UMW values of only 200–400 and the parameters R_a and C_f are lower. The end-cut from the

(15) Suzuki, T.; Itoh, M.; Takegami, Y.; Wanatabe, Y. *Fuel* **1982**, *61*, 402.

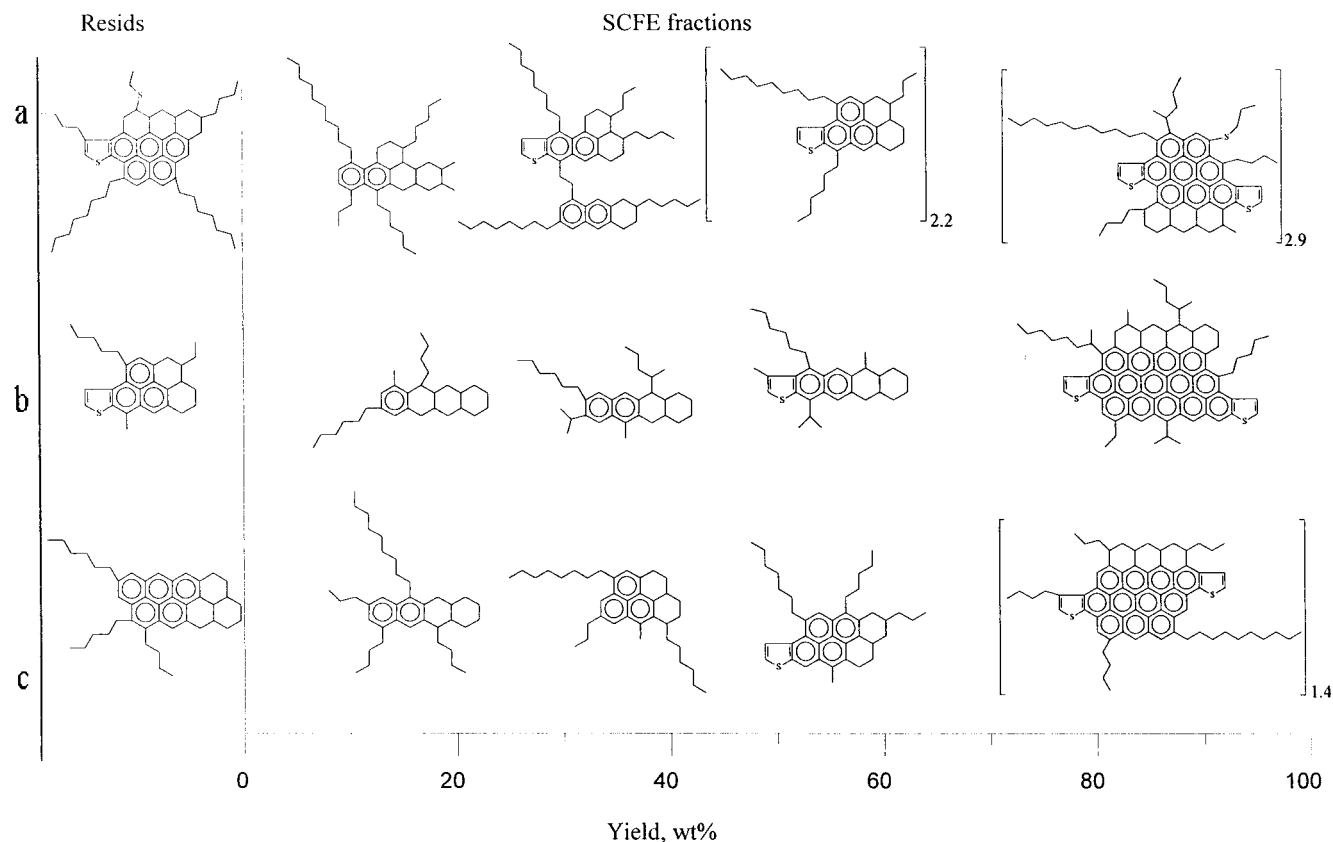


Figure 7. Average structure of resids and their SCFE fractions: (a) P, (b) CK, and (c) HC.

Table 2. Properties of Pitch, HC and CK^a

sample	molecular weight		elemental analysis, (w/w %)						sulfur species (w/w %)	
	M_n	M_w	C	H	N	S	O	H/C	thiophene	sulfide
P	939	2224	80.4	9.3	0.9	6.5	1.0	1.39	4.3	1.4
HC	640	1033	82.7	8.5	1.1	3.9	1.1	1.23	3.2	0
CK	409	577	83.9	8.4	0.8	5.6	1.0	1.20	4.4	0.5

^a There is a systematic difference between the results for total sulfur and carbon by the two methods. XPS (RSD = $\pm 10\%$) tends to underestimate sulfur and overestimate carbon relative to bulk elemental analysis (RSD = $\pm 1\%$). Such discrepancies are not unexpected given the very different nature of the two analytical methods and may result from the greater operator and instrumental biases possible in XPS. Regardless of this disagreement with bulk analysis, the XPS method still offers an excellent approach for determining the amount and distribution of sulfur among different species.

CK material has higher R_a and C_f values than the end-cuts from the P and HC samples; values of R_a and C_f for HC end-cut (HC-EC) are close to those for the heavier fractions P-EC-1 and P-EC-2 from the original pitch.

Figure 7 shows the average structures for selected SCFE front-cuts and the whole end-cut sample from each of the three resids. These calculated structures represent the closest fit to the average molecular parameters detailed earlier. The complexity of the structures clearly increases as the molecules become heavier. The results of chemical analyses for the original residues, prior to SCFE fractionation, are shown in Tables 2 and 3. Molecular weights, H/C ratios, and heteroatom contents for these parent materials show trends similar to those observed for the SCF extracts. However, structural analysis, based on data from each whole residuum, will be dominated by the front-cut fractions. Consequently, the potentially intractable characteristics of the heavy end-cut fractions will not be obvious. This is an important observation as it shows

Table 3. Structural Parameters for Original Resids

structural parameters	vacuum resid		
	virgin bitumen pitch (P)	hydrocracked bottoms (HC)	once-through coking bottoms (CK)
F_a	0.35	0.46	0.48
δ	0.59	0.53	0.53
n	1.1	1	1
USW	840	640	409
C_a	6.7	6.1	5.0
C_{AP}	11.4	11.5	9.5
C_i	8.4	8.6	4.3
C_f	3	3.1	0.9
R_a	5.2	5.3	3.1
m	4.8	3.2	1.2
BI	0.4	0.34	0.41

that bulk analysis can produce an overly optimistic view of residue quality. In this respect, the bulk structures of the original pitches, shown in the left column of Figure 7, give no indication that the residue materials also contain the highly condensed, multi-ring components shown in the right-hand column.

Discussion

Pitch. The front-cut SCFE fractions from virgin bitumen pitch are essentially pentane-soluble material. For these samples there is a general trend for increase in aromaticity and decrease in H/C atomic with yield. This is a reflection of an increase in the number of aromatic rings (R_a) associated with the higher molecular weight fractions. This property is coupled with an increasing degree of condensation (C_f) and decreasing degree of substitution (σ). The majority of carbon present in the aliphatic substituents comprises methylene groups within linear alkane chains. Branched methyl groups are present in relatively small quantities.¹⁶

The end-cut fractions contain "core" structures, comprising condensed polyaromatic rings, associated with heteroatoms (N, thiophenic S) and trace metals (Ni, V). The metals may occur as chelates with porphyrins in the aromatic ring structure as well as with non-porphyrin ligands.¹⁷ These components are typical for pentane-insoluble material. The heavier fractions, P-EC-1 and P-EC-2, contain more than 10 condensed aromatic rings; both of these samples are enriched in metals and heteroatoms relative to the lighter pitch fraction P-EC-3. The latter material comprises less polar molecules with an average of only seven aromatic ring structures. The presence of more than one basic unit is a characteristic of the molecules comprising most of the pitch fractions. These units can be bridged by *n*-alkanes, aliphatic sulfide linkages, and metals.^{17–19}

Overall, cracking reactions lead to the cleavage of aliphatic side chains, bridges, and sulfide linkages. Constituents, such as heavy and light gas oils, having a molecular weight in the range of 180 to 470, are expected as distillates at 524 °C. Pentane-soluble materials from bitumen pitch, i.e., compounds with molecular weights in the 700–1200 range, are likely the main source of this material. Also, there will be some contribution from broken alkyl chains and branches together with fragments, originally linked by sulfur and metals, from the pentane-insoluble end-cut material.¹⁷

Hydro-cracked Residue. Sulfides are almost completely removed during catalytic hydro-cracking. It is of interest to note that the HC fractions have similar unit molecular weights to the corresponding fractions from the original pitch. The unit characteristics R_a and C_f are also similar for HC and P. These results demonstrate that the cleavage of C–S side chains and the breakage of inter-unit bonds are the prevailing reactions in the catalytic hydro-cracking process.

Thermal Cracked Residue. Compared to hydro-cracking, coking is not as efficient at breaking sulfur-carbon bonds. Relative to the front-cut fractions from catalytic hydro-cracking, the equivalent fractions from thermal cracking have lower values for unit molecular weight. Although molecules in the front-cut CK fractions contain fewer aromatic rings, with a lower degree of

condensation than in the original pitch, the overall higher aromaticities and lower H/C ratios in these cases must result from the presence of very short alkyl substituents. The presence of these relatively small molecules may be a manifestation of the greater severity of thermal cracking conditions relative to hydro-cracking.

Process Implications. Free radical formation during thermal cracking is accompanied by condensation reactions.¹⁷ Even though some products of condensation are still soluble in toluene they remain with the residue. Examples are the highly aromatic CK-EC components formed from various fragments of both pentane- and toluene-soluble material. Condensation reactions involving heavy "core" molecules from P-EC lead to formation of coke. Sub-fractions P-EC-1 and EC-2, enriched in thermolysis enhancing components, such as Ni, V, and heterocyclic nitrogen, are the major coke precursors.^{17,20,21} The dramatic reduction in the Ni and N contents of CK-EC relative to P-EC is a reflection of these processes.

In the catalytic hydro-cracking process, most of the C–C bond ruptures can occur through the same free radical mechanism described for the thermal cracking process.³ However, the presence of catalyst activates hydrogen to promote capture of free radicals, thereby reducing polycondensation reactions involving aromatic "core" molecules and subsequent coke formation. The absence of toluene-insoluble organic matter in the HC-EC fraction suggests that the extension of condensation reactions is insignificant. Single-unit, highly aromatic, polar "cores" in P-EC-1 and -2 from bitumen pitch appear to remain pentane-insoluble and thus probably constitute most of the HC-EC fraction. This notion is supported by the structural parameter data together with the metals (Ni and V) and heteroatoms (N) contents for these fractions. These components are ultimately converted to coke, or pseudo-solid species, when subjected to the thermal treatment encountered in coking or severe hydrocracking.²² Compared to the heavier P-EC fractions, the relatively small, single-unit molecules in P-EC-3 have lower aromaticity and polarity and are more likely to be upgraded to pentane-soluble material. Hence, their upgraded products are more likely to report with the HC front-cut fractions.

Conclusions

The presence of more than one basic unit is a characteristic of the bitumen molecules comprising most of the P fractions. The end-cut contains "core" structures, comprising condensed polyaromatic rings, associated with heteroatoms and trace metals.

The cleavage of C–S side chains and the breakage of inter-unit bonds are the prevailing reactions in the catalytic hydro-cracking (HC) process; coking (CK) is not as effective at breaking C–S bonds. Relative to the front-cut fractions from the catalytic hydro-cracking residue, the equivalent fractions from thermal cracking

(16) Mojelsky, T. W.; Montgomery, D. S.; Strausz, O. P. *AOSTRA J. Res.* **1986**, *1*, 177.

(17) Speight, J. G. *The chemistry and technology of petroleum*; Marcel Dekker Inc.: New York, 1991.

(18) Waldo, G. S.; Mullins, O. C.; Penner-Hahn, J. E.; Cramer, S. P. *Fuel* **1992**, *71*, 53.

(19) Strausz, O. P. *Preprints of 4th UNITAR conference on heavy crude and tar sands*, Paper No. 96, 1988.

(20) Speight, J. G. *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.* **1987**, *32*, 413.

(21) Yen, T. Y. *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.* **1983**, *28*, 691.

(22) Le Page, J. F.; Dugert, M.; Billon, A. *Proceedings of the International Conference and Exhibition on Petroleum Refining and Petrochemical Processing*; Beijing, China, September, 1991.

have lower values for unit molecular weight. Molecules in the CK front-cut fractions contain fewer aromatic rings with a lower degree of condensation than those in the original pitch. However, these fractions show overall higher aromaticities and lower H/C ratios because of the shorter alkyl substituents occurring in these molecules.

The highly aromatic CK-EC components are likely to be formed from condensation reactions involving various fragments of pentane- and toluene-soluble material. Condensation reactions involving heavy "core" molecules from P-EC lead to formation of coke.

In the catalytic hydro-cracking process single unit, highly aromatic, polar "cores" from P-EC-1 and EC-2 from bitumen pitch appear to remain toluene-soluble (pentane-insoluble) and thus constitute most of the HC-EC fraction. These coke precursors will be converted to coke, or pseudo-solid species, if subjected to the thermal treatment encountered in coking or severe hydro-cracking.

Acknowledgment. The authors thank G. Pleizier for XPS analysis. Financial assistance from AOSTRA is gratefully acknowledged.

Nomenclature

BS = bitumen-associated solids

CK = vacuum residue from a commercial once-through fluid coking test

CK-EC = end-cut from coking residue

EC = End-cut

GPC = gel permeation chromatography

HC = vacuum residue from a commercial catalytic hydro cracking test

HC-EC = end-cut from hydro cracking residue

M_n = GPC number average molecular weights

M_w = GPC weight average molecular weights

SCFE = super critical fluid extraction

P = virgin bitumen pitch from vacuum distillation

P-EC = end-cut from virgin bitumen pitch

P-EC-1,2,3 = fractions of P-EC separated using toluene/pentane blends

VPO = vapor pressure osmometry

XPS = X-ray photoelectron spectroscopy

EF0001538