

Coking Behaviour During Visbreaking

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Summary

Previously, nuclear magnetic resonance (NMR) carbon-type-analysis data were used to develop a mathematical model of mild thermal conversion (visbreaking) of Athabasca bitumen (Chan et al. 2006). In that work, the major reaction pathways followed during visbreaking were identified. This approach is being extended in the current work to model the visbreaking behaviour of five different oils from different geographical locations around the world. This paper shows the correlation of residue conversion with the contents of different carbon types for five heavy oils from four continents.

During visbreaking runs, operators intend to maximize process yields. This is achieved through increasing process severity by raising temperature. However, if the temperature is too high, coke forms. This maximum temperature varies with different crude oils; therefore, as refinery feedstock composition changes, so does the onset of coking temperature. Coke is a hydrocarbon material that has low hydrogen content and is insoluble in the oil. Consequently, this precipitates in the reactor, eventually causing an unscheduled unit shutdown. We have found that contents of specific carbon types in the feed oils correlate with coke formation. This correlation allows prediction of the quantities of coke that will form under the chosen visbreaking (mild thermal) conditions and the “maximum” quantities of coke that would form under coking (severe thermal) conditions.

Introduction

Thermal conversion is one of the main primary processing technologies used for the upgrading of petroleum feedstocks throughout the world. This accounts for approximately 58% of worldwide-installed capacity for residue upgrading. The other technologies used are hydroconversion and residue fluid catalytic cracking (RFCC). The two thermal conversion technologies used commercially include coking and visbreaking (Sapre 2004). Coking units, which include delayed coking, fluid coking, and flexicoking, have been on the rise worldwide because of the shift to heavy and sour crude oils (Marano 2003). However, with more than 150 units operating around the world, visbreaking still accounts for more than one-quarter of the residue-upgrading capacity of the world (Sapre 2004; Visbreaking 1996). Fuel oil is approximately 18% of the petroleum products worldwide (van den Berg 2000). Production of stable fuel oil with a maximum viscosity reduction is the process objective of a typical visbreaker unit. Through mild thermal cracking, which lowers the viscosity of the fuel oil and reduces the cutterstock demand for viscosity cutting of fuel/oil product, visbreaking increases the net distillate yield of the refinery. All this is achieved at a significantly lower cost than other residue-upgrading processes (e.g., RFCC or hydroconversion) that require high catalyst consumption and high hydrogen consumption. Thus, it is the simplicity of a visbreaker unit that makes this technology the mainstay of numerous petroleum refineries. The run length of the unit is decreased by coking in furnace coils and the soaker drum of visbreaker units. Thus, the main intention is to operate the unit with maximum conversion and minimum coking. Being the most mild and the least complex of the thermal cracking

technologies, visbreaking is the logical first step in the direction of studying and modelling the thermal cracking process.

Petroleum fractions that are fed to visbreaker units are complex mixtures of thousands of hydrocarbon molecules that are impossible to identify individually. Therefore, chemistry of petroleum upgrading is usually studied by dividing the feedstock into lumps on the basis of physical properties [(e.g., molecular weight, API gravity, and boiling point (BP)]. The limitation of pseudocomponent lumping based only on volatility or boiling range is that the organic compounds of different molecular types (e.g., paraffins, naphthenes, and aromatics) are collected in a lump, although they are known to have different reactivity during thermal cracking (Quann and Jaffe 1992). Likewise, the limitation of lumping based only on the solubility classes, such as in saturates, aromatics, resins, and asphaltenes (SARA) classification, is that molecules of similar types but of different sizes are lumped. Therefore, the present work used a new pseudocomponent definition that combines both the boiling ranges and the solubility classes. Thus, the feed is represented by eight pseudocomponents and the product by nine pseudocomponents. The list of pseudocomponents is given in **Table 1**. The new pseudocomponent definition allows feed characterization into groups of different chemical reactivity in a significantly better fashion. For example, separation of “aromatics” in naphtha, gas oil, and residue allows separation of aromatic species with low nitrogen content into different molecular-size groups.

In the present work, NMR spectroscopy has been used to characterize five heavy oils from around the world and their products from visbreaking to aid understanding of the pathways followed during mild thermal conversion. Because the chosen process conditions resulted in coke formation in the products, the contents of carbon types that correlate with coke formation were also identified. All calculations were performed on a 1 kg of feed basis.

Carbon Types

Petroleum is a complex mixture of hydrocarbon molecules. The chemical and physical properties of a hydrocarbon molecule depend on how a carbon atom in the molecule is bonded to other carbon, hydrogen, and hetero-atoms. Bonding, or the sharing of electrons by the carbon atoms among themselves or with other elements, determines the “type” of carbon. A complex hydrocarbon molecule has numerous different carbon types. Examples of different carbon types include aromatic, naphthenic, olefinic, paraffinic, and branched paraffinic carbon. The C-C or C-H bonds formed by different carbon types will have different bond-dissociation energies; thus, their stability and reactivity under thermal cracking conditions will differ. Thermal cracking is a free-radical mechanism. Free radicals are formed upon bond breaking where one electron is shared by each fragment. This type of bond breaking, which occurs during thermal cracking, is called homolysis and the energy is called homolytic bond-dissociation energy.

Thermal stability of petroleum hydrocarbons is dependent upon the bond-dissociation energy of the carbon-carbon, carbon-hydrogen, and carbon-sulphur bonds. The bond-dissociation energy depends on the extent of overlap of the atomic orbitals of the nuclei and is affected by various factors [e.g., resonance stabilization (aromatic bonds) and different types of bond strain]. The carbon-carbon bond cleavage in a benzene ring is not possible in mild thermal cracking because of the resonance structure, which accords extra stability to the benzene ring (as compared with cyclohexatriene) (Morrison and Boyd 1987). Instead, carbon-carbon cleavage is significantly more likely in the alkyl chains attached to the aromatics. The CH₂ of an alkyl chain attached to an aromatic carbon in a

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This paper (SPE 161014) was accepted for presentation at the Petroleum Society of Canada's Eighth Canadian International Petroleum Conference (58th Annual Technical Meeting), held in Calgary, 12–14 June 2007, and revised for publication. Original manuscript received for review 18 June 2007. Revised manuscript received for review 30 May 2011. Paper peer approved 14 April 2012.

TABLE 1—LIST OF PSEUDOCOMPONENTS

Feed	Product
Naphtha (IBP*–204°C)	Gas (C4 –)
Gas oil (204–524°C)	Naphtha (204°C–)
- Saturates	Gas oil (204–524°C)
- Aromatics	- Saturates
- Polars	- Aromatics
Residue (524°C+)	- Polars
- Saturates	Residue (524°C+)
- Aromatics	- Saturates
- Polars	- Aromatics
- Asphaltenes	- Polars
	- Asphaltenes

*IBP = Initial Boiling Point

polyaromatic hydrocarbon (PAH) molecule is less stable than that attached to an aromatic carbon of a monoaromatic ring. Van Speybroeck et al. (2006) have classified the PAHs into six groups on the basis of the number of rings and have shown that the bond-dissociation energy of alkyl chains attached to condensed ring aromatics is lower because of less stability of the molecule caused by steric hindrance. This renders their free radicals more stability because of relief of steric hindrance. Through calculation of relative-rate constants of the cleavage of alkyl chains from condensed naphthenic hydrocarbons, Berman and Petrov (1983) concluded that the thermal stability of the cycloparaffins decreases as the number of rings and length of chains increase, while the type of ring chain also has a bearing on the rate of cracking.

NMR spectroscopy plays a prominent role in the structural analysis of petroleum fractions. Both proton (^1H) and carbon (^{13}C) NMR spectra can be used to quantify different carbon types present in oil. Thus, the carbon-type content of the pseudocomponents before and after cracking can be measured. Because carbon type actually means carbon “bond” type, the information reveals the net chemistry that has occurred during the process. Carbon-type analysis in this fashion quantifies the interconversion of one carbon type into another during cracking. Depending upon the contents of particular carbon types in a visbreaker feed, the “crackability” of the feed can be predicted.

Experimental Work

The present work is intended to validate the approach used previously for developing a mathematical model for visbreaking by applying the same approach to five heavy oils representing feedstocks with different thermal reactivity from across the world. For this, thermal cracking of each feedstock was performed in a 1-L continuously stirred tank reactor autoclave where two runs were performed using 400 g of feed. The reactor was flushed with nitrogen before heating and reached a maximum pressure in the range of 300 to 500 psig at temperature (405°C), depending on gas-make. The run time was 30 minutes. The volume of gas was measured by a gas meter because the gas was transferred into a gas bag at room temperature (20°C). The contents of the gas products are the averages of the results for two runs for each feedstock. The total liquid products (TLP) for the two runs were combined and sent for analyses.

Fraction Preparation. The feed and TLP were fractionated into naphtha (BP<204°C), gas oil (BP of 204–524°C), and residue (BP>524°C) using the American Society for Testing and Materials (ASTM 2001) D1160 method. Asphaltenes were precipitated from the D1160 vacuum residue (BP>524°C) with pentane, using a single treatment of the procedure outlined in Peramanu et al. (1999). The gas-oil and the residue maltenes were separated into saturates, aromatics, and polar fractions using a modification of the clay/gel-adsorption-chromatography method described in Peramanu et al. (1999).

Characterization of Pseudocomponents. Gas Analysis. The gas analysis was run on the gas product on either a refinery gas analyzer or an Agilent Technologies 3000A gas-chromatography (GC) instrument.

Elemental Analysis. Sulphur contents of naphtha were measured using X-ray fluorescence (ASTM D4294) on a Horiba XR Fluorometer (SLFA-1800). The sulphur content of the gas oil saturates were measured by GC (HP 6890) using sulphur chemiluminescence detection (ASTM D5623). The sulphur contents of all other samples was measured using a Leco SC 432 analyzer, where ASTM D1552 was used for the aromatics and polars and ASTM D4239 was used for asphaltenes. The nitrogen contents of the naphtha and saturates were measured using the ASTM D4629 method on a Dohrman nitrogen analyzer (DN-1000). The carbon and hydrogen content of saturates was measured using the ASTM D5291 method on a Perkin Elmer 2400 analyzer. The carbon, hydrogen, and nitrogen contents of the aromatics, polars, and asphaltenes were measured on a Leco 1000 analyzer using ASTM D5291 for the aromatics and polars and ASTM D5373 for the asphaltenes. The carbon and hydrogen content of the naphtha was measured on the Leco 1000 analyzer using the ASTM D5291 procedure.

Coke Content. Conradson carbon content of the feed and TLP was measured using the microcarbon-residue (MCR)-test procedure (ASTM D4530). The toluene insolubles contents, which include both hydrocarbon and inorganic components if present, were obtained by soxhlet extraction of the feed or TLP residue (BP>524°C) using ASTM D4072.

NMR Spectroscopy. ^1H NMR samples were prepared by mixing approximately 20 mg of the sample with 700 μL deuteriochloroform (CDCl_3). For ^{13}C NMR spectra, approximately 50 mg of asphaltenes and 100 mg of all other fractions were used in either 700 μL or 600 μL CDCl_3 , respectively. The NMR experiments were performed at room temperature ($20\pm 1^\circ\text{C}$) on a Varian XL-300 NMR spectrometer, operating at 299.943 MHz for proton and 75.429 MHz for carbon.

The proton spectra were collected with an acquisition time of 2.1 seconds, a sweepwidth of 7,000 Hz, a pulse flip angle of 30.8° (8.2 μs), and a 1-second recycle delay. These pulse/recycle conditions permit the collection of quantitative spectra for all protonated molecular species in the petroleum samples where the maximum spin lattice relaxation time (T_1) is expected to be less than 20 seconds. The spectra, resulting from 128 scans and using 0.3-Hz line broadening, were referenced to the residual chloroform resonance at 7.24 ppm.

The quantitative carbon spectra were acquired using an acquisition time of 0.9 seconds and a sweepwidth of 16,500 Hz. For naphtha and gas oil samples, a flip angle of 26.2° (4.6 μs) and recycle delay of 10 seconds were used, and for the residue samples, a flip angle of 31.9° (5.7 μs) and a 4-second delay were used. These parameters are quantitative for carbons with spin lattice relaxation times (T_1) on the order of 100 seconds in distillate and 30 seconds in the residue. Reverse-gated waltz proton decoupling was used to avoid nuclear Overhauser effect enhancements of the carbon signals. The spectra were the result of 5,000 scans for the naphtha and gas oil fractions (BP<524°C) and 15,000 scans for the residue fractions (BP>524°C). Line broadening was used to improve the signal/noise ratio of the spectra. Naphtha and saturates spectra used 5-Hz, aromatics and polars spectra used 10-Hz, and asphaltenes spectra used 15-Hz line broadening. All spectra were referenced to the CDCl_3 resonance at 77.0 ppm.

Carbon-type analyses were performed using proton and carbon NMR spectra and elemental analysis results, using a procedure based on that described by Japanwala et al. (2002).

Results and Discussion

The visbreaker feeds investigated in this work were chosen to represent different geographic regions of the world and included heavy oils from Alberta, the Middle East, the United States, Asia, and South America. The percentage conversion in a visbreaker unit can be reported as the yield of gas and naphtha or given by the quantity of residue (524°C+) present. The percentage

	S. American Oil	Middle Eastern Oil	Alberta oil	Asian Oil	US Oil
Resid (524°C+)	0.8	30.4	38.4	15.5	28.5
Resid Saturates	-0.2	41.6	43.9	-2.0	36.7
Resid Aromatics	-3.5	44.7	41.5	18.6	37.1
Resid Resins	5.5	45.8	65.4	31.8	38.9
Resid Asphaltenes	2.2	-16.5	16.2	-6.6	-12.3

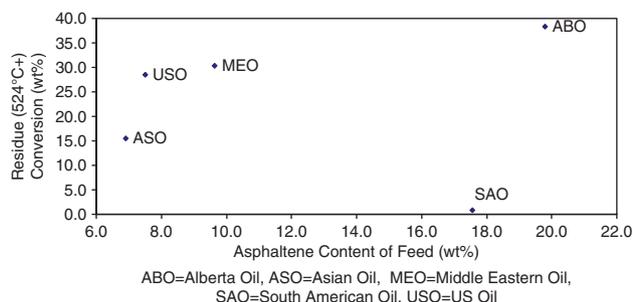


Fig. 1—Residue conversion vs. asphaltene content of feed.

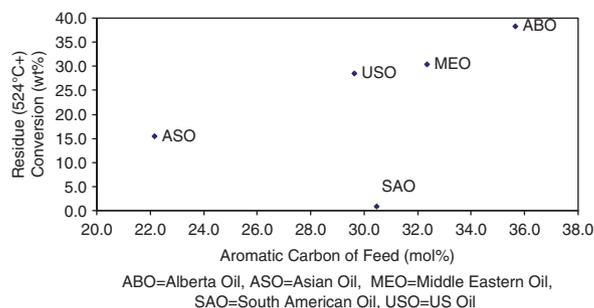


Fig. 2—Residue conversion vs. aromatic carbon of feed.

conversion of all five oils, as measured by the quantity of residue (524°C+) present, is reported in **Table 2**. The percentage residue conversion in a visbreaker has been related to asphaltene content, saturate content, and the aromaticity of the feed (Akbar and Geelen 1981). Under similar thermal conditions, the residue conversion in the Alberta oil was the highest, followed by the Middle Eastern, US, and Asian oils, while the South American oil practically did not convert. In this case, residue conversion does not correlate with the asphaltene content of the feed, as shown in **Fig. 1**. In **Fig. 2**, residue conversion seems to correlate with the aromatic carbon content in the feed, but there is no explanation for the almost zero conversion of the South American oil, having a significant 30.4% aromatic carbon content. An important observation from the data is that under similar reaction severities, the percentage conversion of the respective pseudocomponents varies from feed to feed (**Fig. 3**). For instance, the conversion of residue saturates varies from 43.9% in Alberta oil to -2.0% in the Asian oil. The difference in conversion is even more pronounced in residue polars. While asphaltenes convert to other pseudocomponents in the Alberta oil, there is a net addition to asphaltenes in other oils (**Fig. 3**). These data help reinforce the understanding that these pseudocomponents are not a homogeneous chemical entity and their chemical composition and the reactivity under visbreaking conditions vary from feed to feed. Therefore, the reactivity of

a visbreaker feed cannot be attributed to the individual composition of these pseudocomponents (viz. percentage of asphaltenes, aromatics, or polars present). This complex behaviour by petroleum fractions underscores the importance of the study of carbon types and molecular structure in determining the reactivity of a feed. NMR spectroscopy presents a reliable method for quantification of these carbon types.

NMR Structural Analysis. In the present work, NMR structural analysis was performed on all pseudocomponents before and after cracking. NMR data give content information for more than 80 types of different carbon species including aromatic, cycloparaffinic, branched paraffinic, paraffinic, and olefinic carbon that have been mentioned in the previous work (Chan et al. 2006). In addition, the NMR data reveal the average chain length, the aromatic- and naphthenic-ring cluster sizes, and the α -to-aromatic cycloparaffins present in the pseudocomponents. From the perspective of residue conversion to distillates, the most relevant data are those of the residue fraction and its subfractions. A comparison of the NMR-carbon-type information of the residue fraction of the different feeds reveals that the average aromatic cluster size varies from 13 carbons (two to three rings) to 20 carbons (four to five rings), where the largest clusters are present in the South American oil. The average cycloparaffinic-ring cluster size for the

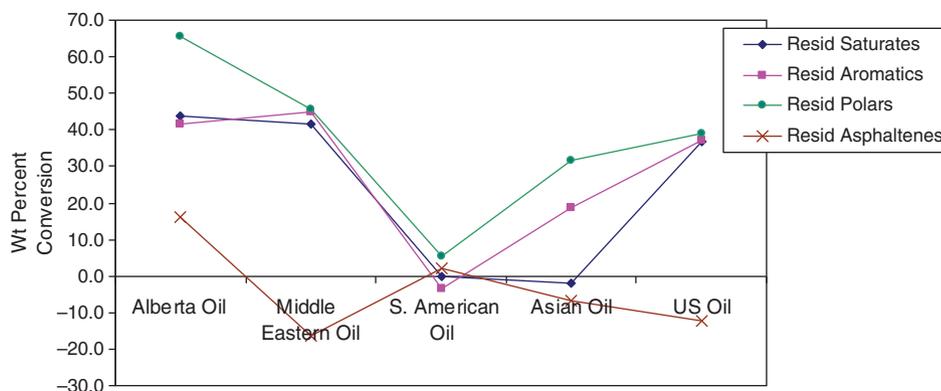


Fig. 3—Wt% conversion for different oils.

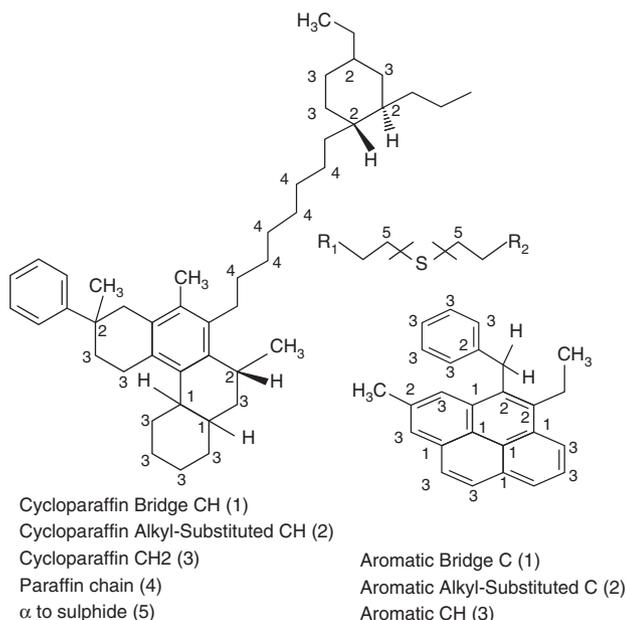


Fig. 4—Molecular structures that illustrate the carbon types quantified using ¹³C and ¹H NMR spectroscopy.

residue varies from seven carbons (one to two rings) to 11 carbons (two to three rings), with the largest clusters being present in the US oil. A comparison of the chain segment lengths in the residue fractions shows that the average length varies from 3.8 to 7.5 carbons, where the longest chain segments are in the Asian oil. Apart from the information on the relative amount of carbon types present in the residue fraction of the feed, the NMR data also point out the degree of participation of different carbon types in thermal cracking reactions from the net change of these carbon types before and after cracking. To help understand the potential contribution of different carbon types to the reactivity of the different oils, pyrolysis studies of model compounds under visbreaking conditions were reviewed.

Pyrolysis of Model Compounds. The literature provides numerous examples of pyrolysis of model compounds conducted at similar reaction severities. Three classes of model compounds that are relevant to visbreaking reactions at the experimental severity were reviewed. The knowledge of kinetic data, reaction products, and pathways of pyrolysis of these model compounds provides insight into the chemical behaviour of identical moieties present in the visbreaker feeds. The NMR data provide the contents of specific types of carbon in the feed and products that could/should be involved with thermal conversion (Savage et al. 1989).

Polycyclic Alkylaromatics. Pyrolysis of alkylaromatics has been investigated extensively (Savage et al. 1989; Smith and Savage 1991a, 1992; Savage and Klein 1987). Use of kinetic data from this literature reveals that the mol% conversion of the alkylaromatic model compounds at process severity similar to the current experimental conditions varies from 20 to 99%. The different reaction products result by thermal cleavage of C-C bonds, primarily at the β position of the chain relative to the ring or at the aryl-alkyl (α) position. Smith and Savage (1991a) have shown that the reactivity has some dependence on alkyl chain length. In particular, reactivity sharply increases from chain length one to five, after which chain length plays a minor role in overall reactivity.

Polycyclic Alkylcycloparaffins. Model compounds representative of alkyl-substituted polycyclic alkylcycloparaffins moieties in oil have also been studied for their pyrolysis behaviour (Savage and Klein 1988; Humburg and Savage 1996; Mizan et al. 1997;

Savage et al. 1997). Under identical reaction conditions, mol% conversion of these model compounds varies from 10 to 40%, having lower kinetic constants at similar temperatures than their polycyclic alkylaromatics equivalents. Major reaction products are produced by dealkylation at or near the ring and little dehydrogenation is observed at identical reaction severity. Savage et al. (1997) have shown that the reactivity of polycyclic alkylcycloparaffins increases with the chain length and number of cycloparaffin rings.

Diphenyl Alkanes. α,ω-diphenylalkanes are relevant model compounds to represent polyaromatic species linked by paraffin chains in heavy oils (Smith and Savage 1991b). The kinetic data of these model compounds reveal a mol% conversion from more than 94% to 100% under identical reaction conditions. The reaction products are produced by cleavage of C-C bonds at the aryl-alkyl position or at other positions near the ring. The pyrolysis of 1,3-bis(1-pyrene) propane is an example of a residue molecule converting to other residue molecules after thermal cleavage of aliphatic linkage (Smith and Savage 1991b).

Residue Conversion Model

The percent conversion in visbreaking from residue fraction (524°C+) to distillate involves cracking to lighter products whose BP falls in the range of gas oil (204–524°C), naphtha (IBP–204°C), or gas.

From the model compound studies, the most important pathways for conversion of heavy oils during visbreaking are the side chain cleavage. The higher the alkyl substitution at the aromatic and possibly naphthenic rings, the higher the reactivity. Also, the C-S bonds in the chains are weaker than other aliphatic bonds and are important cleavage sites (Gray 1994). Thus, the residue conversion should be dependent upon the number of alkyl substituted aromatic and cycloparaffinic carbon types and the sulphide sites in chains. Another factor that directly affects residue conversion is the chain length. It is known that the reactivity of alkylaromatic model compounds linearly increases with the chain length and then maximizes at chain length approaching five carbon atoms. Typical carbon types and those that directly affect residue conversion are shown in Fig. 4.

Previous work (Chan et al. 2006) suggested that side-chain cleavage of cycloparaffin species is minor because of the small ring cluster sizes (mostly one to two rings). Because the oils in this study have similar cycloparaffin cluster sizes, it is expected that cleavage of their side-chains will also have a lower contribution [this expectation was supported in that when the content of alkyl-substituted cycloparaffinic carbon was included in the residue-reactivity-index (RRI) calculation, the correlation with residue conversion was lower].

Consequently, the contents of alkyl-substituted aromatic and sulphidic carbon and average chain lengths results were consolidated through formulation of an RRI as

$$RRI = (A \times B) + C, \dots \dots \dots (1)$$

where *A* is the content of alkyl substituted aromatic carbon (moles), *B* is the minimum (1, Alkyl chain length/5), and *C* is the content of α-to-sulphides (moles), on a 1 kg of feed basis.

The residue wt% conversion was found to correlate with RRI with a correlation coefficient (*R*²) of 0.93 (Fig. 5). It is to be noted that the South American oil which had the lowest residue conversion, has the least alkyl substitution and the shortest chains. This appears to be the reason that there was low residue conversion, despite high aromatic content.

Coke Formation in Thermal Cracking. Conradson carbon (otherwise known as MCR) content of oil is the most useful indicator of its coke-formation tendency during a severe thermal cracking process (e.g., coking). The MCR of various asphaltenes has been found to be dependent on their NMR-derived aromatic

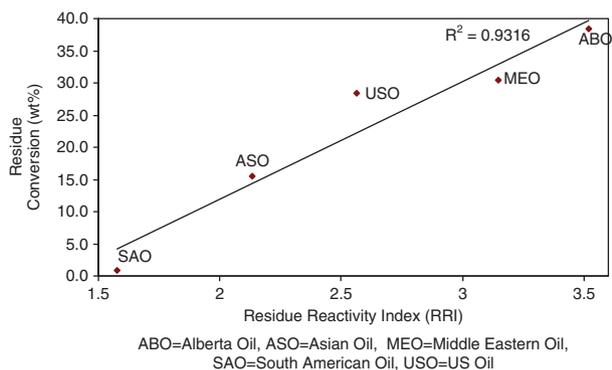


Fig. 5—Residue conversion vs. residue reactivity index.

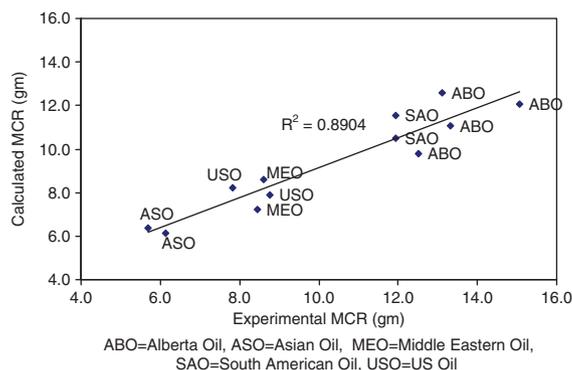


Fig. 6—Calculated MCR vs. experimental MCR.

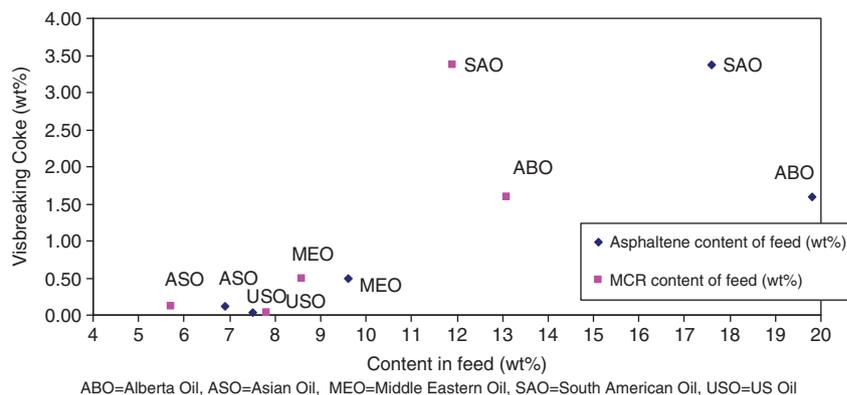


Fig. 7—Visbreaking coke vs. content in feed.

carbon content (Gray 2003). With the availability of detailed NMR and elemental data for all pseudocomponents of feed and products of visbreaking, the MCR content of these oils was calculated as the sum of aromatic carbon of residue polars and asphaltenes. Fig. 6 shows the comparison of the experimental and calculated MCR values of the different feed and products. The correlation coefficient for the data is 0.89. The correlation is consistent with the hypothesis that after cracking of side chains, the aromatic carbon of polars and asphaltenes in the residue fraction are the major species that form coke.

While MCR is a good indication of coke formation during coking, the coke formation during visbreaking does not correlate with the MCR content of the feed (Fig. 7). Coke formation during visbreaking is measured by the toluene insolubles content of the visbreaking product. Comparing the toluene insolubles after visbreaking of the five different feeds provides an insight into their coking tendencies close to the onset of coking. The maximum coke formation was observed in the South American oil, which has almost no residue conversion (Table 3).

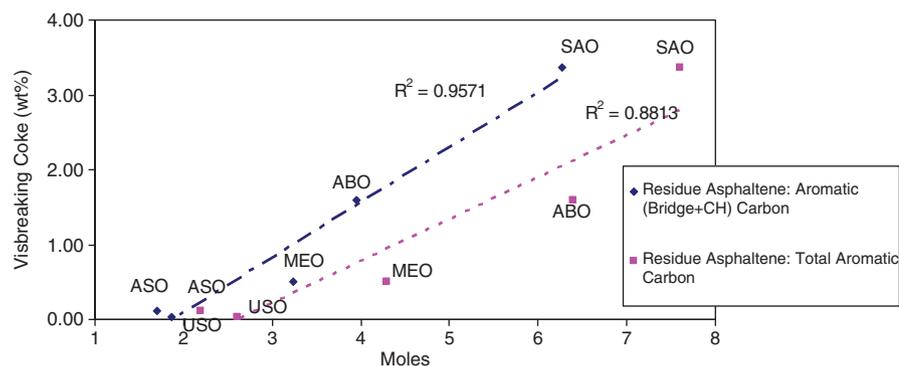
Coking propensity, which is the ratio of the coke yield to the process severity, has been found to correlate well with the asphaltene content of the feed (Yan 1990, 1987). The calculation of process severity for coke formation requires the energy of activation for coking. The present visbreaking runs were performed at a similar severity, and for this reason we do not have sufficient data to estimate the energy of activation. From Fig. 7 we can see that feed asphaltene contents do not correlate with the toluene insol-

bles after visbreaking. Analysis of the contents of carbon types of the residue asphaltenes shows that the number of moles of aromatic bridge and protonated aromatic (CH) carbon in the feed correlates directly with the contents of coke generated under the current conditions (correlation coefficient of 0.96) (Fig. 8). The contents of total aromatic carbon do not correlate as well (correlation coefficient of 0.88). Because coke formation under visbreaking conditions is close to the onset of coking, these results show that the least-soluble species, the largest polyaromatics with the least alkyl substituents, will be the most likely to “fall out of solution” after one or two side-chain bonds are broken. Note that in all our previous discussions we have attempted to fit only linear models.

Conclusions

The study of thermal cracking through carbon-type analysis helps to unravel the complex nature of petroleum feedstocks and offers an opportunity to correlate petroleum chemical structure with its behaviour during physical and chemical processes. The reactivity of different visbreaker feeds, including their coking behaviour, can be attributed to their chemical compositions as quantified using NMR carbon-type analyses. The present work is part of a project to develop a mechanistic mathematical model for mild thermal cracking. Future work entails validation of the existing visbreaking mathematical model with the carbon-type analysis data for two more feeds under different severities. The overall

S. American Oil	Middle Eastern Oil	Alberta oil	Asian Oil	US Oil
3.37	0.50	1.59	0.11	0.03



ABO=Alberta Oil, ASO=Asian Oil, MEO=Middle Eastern Oil, SAO=South American Oil, USO=US Oil

Fig. 8—Visbreaking coke vs. moles of different carbon types, (based on 1 kg of feed).

goal is to create a full model to be able to describe the behaviour of all petroleum feedstocks under all visbreaking severities.

Acknowledgements

This research is supported by the Natural Sciences and Engineering Research Council (NSERC), the Department of Chemical and Materials Engineering at the University of Alberta, and the National Centre for Upgrading Technology (NCUT) through partial funding by the Canadian Program for Energy Research and Development, the Alberta Research Council, and the Alberta Energy Research Institute. The authors wish to acknowledge Allison Ross and Sara Salmon for running the visbreaking project and performing SARA separations. As well, the authors would like to thank David Patmore and Wayne Mah for performing the auto-clave runs, and the NCUT Analytical Group for performing the distillations and analyses.

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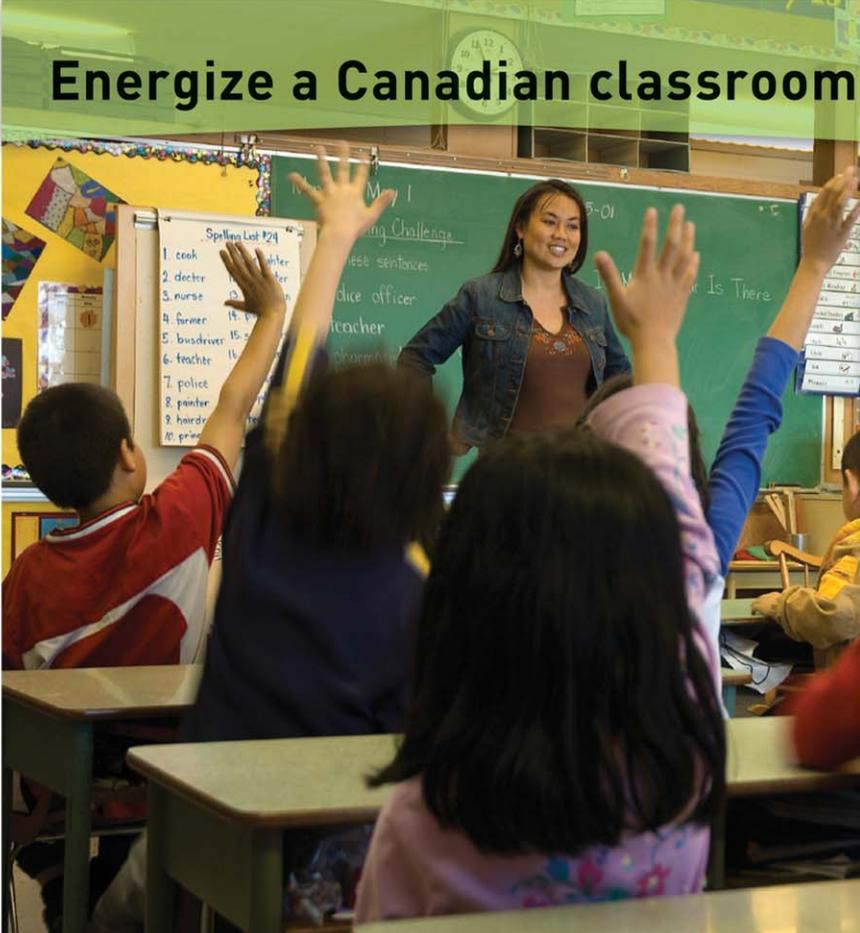
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