Mathematical Modeling of Visbreaking Process

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Abstract

Visbreaking is a mild thermal cracking process to reduce the viscosity of heavy oil residues. Previously, nuclear magnetic resonance (NMR) carbon-type analysis data were used to model visbreaking of Athabasca bitumen [1], where the major reaction pathways during visbreaking were identified. The present work extends the same approach further to explain the visbreaking behavior of six different oils.

In the current study, the visbreaking of these oils was performed at a single severity in an autoclave and the feed and the products were lumped on the basis of polarity and boiling point ranges, allowing their separation into pseudo-components of different chemical reactivity. The quantification of carbon types in these pseudo-components was done using elemental analyses and nuclear magnetic spectroscopy. Four classes of representative model compounds were chosen based on the carbon-type data of the pseudo-components. A literature review of the pyrolysis studies of these model compounds suggested the major types of reactions involved during visbreaking. Through the use of reaction pathways and model rules, model correlations were able to predict the residue conversion, coke formation and product yields during visbreaking.

Introduction

Thermal conversion is one of the primary processing technologies used for the upgrading of petroleum feedstock all over the world. It accounts for approximately 58 percent of worldwide installed capacity for residue upgrading. The other technologies used are hydroconversion and residue fluidized catalytic cracking (RFCC). The two thermal conversion technologies used commercially include coking and visbreaking[2]. Coking units, which include delayed coking, fluid coking and Flexicoking have been on the rise worldwide because of a shift to heavy and sour crude oils [3]. However, with more than 150 units operating around the world, visbreaking still accounts for more than a quarter of the residue upgrading capacity of the world [2, 4].

Fuel oil is approximately 18 percent of the petroleum products worldwide[5]. Production of stable fuel oil with maximum viscosity reduction is the process objective of a typical visbreaker unit. The run-length of the unit is decreased by coke formation in the furnace coils and the soaker drum. Therefore, the main aim is to operate the unit with maximum conversion and minimum coking. Through mild thermal cracking, which lowers the viscosity of the heavy distillates and reduces the cutterstock demand for viscosity cutting of the fuel oil product, visbreaking increases the net distillate yield of the refinery. All this is achieved at a much lower cost than other residue upgrading processes like RFCC or hydroconversion that require high catalyst and high hydrogen consumption, respectively. Thus, it is the simplicity of a visbreaker unit that

makes this technology the mainstay of many petroleum refineries. Visbreaking is the mildest and the least complex of the thermal cracking technologies. Therefore it is the logical first step in the direction of studying and modeling of the thermal cracking process.

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 many different carbon-types. Examples of different carbon-types include aromatic, naphthenic, olefinic, paraffinic and branched paraffinic carbon. NMR spectroscopy plays a prominent role in the structural analysis of petroleum fractions. Both proton (1H) and carbon (13C) NMR spectra can be used to quantify different carbon-types present in oil. Thus, the carbon-type content of the pseudo-components before and after cracking can be measured. As carbon-type actually means carbon bond type, the information can be used to reveal the net chemistry that has occurred during the process. Carbon-type analysis in this fashion quantifies the inter-conversion 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 also be predicted. In the present work, NMR structural analysis is performed on all pseudo-components before and after cracking. NMR data gives content information for over 80 types of different carbon species including aromatic, cycloparaffinic, branched paraffinic, paraffinic, and olefinic carbon. In addition, the NMR data reveals the average chain-length, the aromatic and naphthenic ring cluster sizes and the α-to-aromatic cycloparaffinic carbon present in the pseudo-components.

Previously, nuclear magnetic resonance (NMR) carbon-type analysis data were used to develop a mathematical model of mild thermal conversion (visbreaking) of Athabasca bitumen, where the major reaction pathways followed during visbreaking were identified. This approach has been extended in the current research to model the visbreaking behavior of six petroleum oils from different geographical locations around the world. These six oils include two from Western Canada and one each from the USA, Middle East, South America and Asia. In particular, the objective of this research is to advance the understanding of chemistry involved during visbreaking process by proposing rule-based correlations, based on feed carbon type data and the visbreaking reaction pathways, for predicting product (gas and liquid) yields, percentage residue conversion and coke formation during visbreaking at a single severity.

The experimental work was performed at the National Centre for Upgrading Technology (NCUT), Devon, Alberta.

Experimental Visbreaking Conditions

Thermal cracking of each feedstock was performed in a 1-liter continuous stirred-tank reactor (CSTR) autoclave where two runs were performed using 400 grams of feed. The reactor was flushed with nitrogen prior to heating and reached a maximum pressure of in the range of 300-500 psig at the temperature 405°C, depending on the gas-make. The run time was 30 minutes. The volume of gas was measured by a gas meter as the gas was transferred into a gas bag at the room temperature of 20°C. The contents of the gas products are the averages of the results for two runs under same conditions for each feedstock. The total liquid products for the two runs were combined and analysed.

Fraction Preparation

The feed and total liquid product (TLP) were fractionated into naphtha (IBP-204°C), gasoil (204-524°C), and residue (524°C+) using the American Society for Testing and Materials[6] (ASTM) D1160 method. The separation of these fractions into saturates, aromatics, resins or polars and asphaltenes (SARA) was done using the following procedure. Asphaltenes were precipitated from the D1160 vacuum residue (524°C+) with pentane, using a single treatment of the procedure outlined in Peramanu et al. [7]. The gasoil 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. [7]

Characterization of Pseudo-components

Gas Analysis

The gas analysis was run on the gas product on a Refinery Gas Analyzer (MTI).

Elemental Analysis

Sulfur contents of naphtha were measured using x-ray fluorescence (ASTM D4294) on a Horiba XR Fluorometer (SLFA-1800). The sulfur content of the gasoil saturates were measured by GC (HP 6890) using sulfur chemiluminescence detection (ASTM D5623). The sulfur contents of all other samples were 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 as well as polars and ASTM D5373 for the asphaltenes. The carbon and hydrogen content of the naphtha were 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 were obtained by soxhlet extraction of the feed or TLP residue (524°C+) using ASTM D4072.

Nuclear Magnetic Resonance Spectroscopy

1H NMR samples were prepared by mixing approximately 20 mg of the sample with 700μL deuterochloroform (CDCl3). For 13C NMR spectra, approximately 50 mg of asphaltenes and 100 mg of all other fractions were used in either 700μL or 600 μL CDCl3, respectively. The NMR experiments were performed at room temperature (20±1°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 s, a sweepwidth of 7000 Hz, a pulse flip angle of 30.8° (8.2 μs), and a 1-s recycle delay. The spectra, resulting from 128 scans and using 0.33 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 s and a sweepwidth of 16,500 Hz. For naphtha and gas oil samples, a flip angle of 26.2° (4.6μs) and recycle delay of 10 s were used, and for the residue samples, a

flip angle of 31.9° (5.7μs) and a 4-s delay were used. Reverse-gated waltz proton decoupling was used to avoid nuclear Overhauser effect enhancements of the carbon signals. The spectra were the result of 5000 scans for the naptha and gas oil fractions (524°C -) and 15,000 scans for the residue fractions (524°C+). Line broadening was used to improve the signal-to-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 CDCl3 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. [8] The NMR carbon-type data from the residue and gasoil pseudo-components gives quantitative information about the ring sizes and the alkyl chain lengths and thus help in the selection of the representative model compounds.

Representative Model Compounds

The average chain length in the asphaltenes ranges from 3.3 to 6.1 and is shorter than that of the residue aromatics which is from 3.9 to 7.9. The maximum chain length of 8.5 is in the residue saturates fraction in the Asian oil. The maximum aromatic cluster size of 22 carbons is in the asphaltene fraction of the South American oil. The aromatic carbon cluster size in the residue aromatic fraction range from 13 to 21 carbons. The maximum cycloparaffin carbon cluster size of 18 carbons is in the gasoil aromatic fraction in South American oil. The content of α-to-aromatic cycloparaffin species, whose behavior during visbreaking will be suggested by hydroaromatic model compounds, is the maximum in the gasoil polar and aromatic fractions. The complexity of chemistry in these pseudo-components makes simplified generalization about their pyrolysis behavior misleading. The knowledge of the kinetic data, reaction products and pathways of pyrolysis of the representative model compounds provides insight into the chemical behavior of identical moieties present in the visbreaker feeds. The literature provides many examples of pyrolysis of model compounds conducted at similar reaction severity. These model compounds can be classified broadly into four classes of model compounds that are relevant to visbreaking reactions at the experimental severity [9, 10, 11, 12, 13, 14]. These classes are polycyclic alkylaromatics, polycyclic alkylcycloparaffins, 1,3-diarylalkanes and hydroaromatics.

Polycyclic Alkylaromatics

The pyrolysis of alkylaromatics has been extensively investigated by researchers [15, 16, 17, 18]. The kinetic data from this literature reveals that the mole percent conversion of the alkylaromatic model compounds at a process severity similar to the current experimental conditions varies from 20 to 99 percent. Smith and Savage [15] have shown that the reactivity of polycyclic alkylaromatics has a dependence on alkyl chain length and the conversion of alkylpyrene during pyrolysis at 400°C and 120 minutes sharply increases as the chain length increases from one to five, after which the chain length plays a minor role in its overall reactivity.

Smith [10] has shown the reaction network for the pyrolysis of dodecylpyrene. Due to its multi-ring aromatic structure attached to an alkyl chain, dodecylpyrene resembles the polycyclic alkylaromatic moieties present in heavy oil. It is known from the NMR carbon-type data that the maximum value for the average aromatic carbon cluster size in the residue fraction is 22 or 4-5 aromatic rings. Dodecylpyrene reacts by two pathways

which are different due to the position of thermal cleavage of C-C bonds at the ring. The side chain in pathway 1 breaks at the β position, while in pathway 2 breaks off at the strong aryl-alkyl α position. The first pathway is also analogous to the alkylbenzene pyrolysis. Different mechanisms have been proposed to explain the second pathway which involves the breaking of a strong alkyl-aryl bond, but irrespective of the pathways involved the kinetics and reaction network of polycyclic alkylaromatic pyrolysis indicates that these species are the most reactive species under mild conditions, their reactivity depends upon the length of alkyl chains and they react to form different lighter pseudo-components depending upon the length of the alkyl chain and the cluster size of the aromatic ring.

Polycyclic Alkylcycloparaffins

Model compounds representative of the polycyclic alkylcycloparaffins moieties in oil have also been studied for their pyrolysis behavior [12, 19, 20, 21]. Under identical reaction conditions, the mole percent conversion of these model compounds varies from 10 to 40 percent, 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 very little dehydrogenation is observed at identical reaction severity [11, 13]. Savage et al. [11] have shown that the reactivity of polycyclic alkylcycloparaffins increases with the chain length and number of cycloparaffin rings.

1, 3-Diarylalkanes

α,ω-Diphenylalkanes are relevant model compounds to represent polyaromatic species linked by paraffin chains in heavy oils [11]. The kinetic data of 1,3-diaryl-propanes reveals that conversion of 2-(3-phenylpropyl)-naphthalene (PPN) is around 94 percent under reaction conditions similar to the experimental, while that of 1,3-bis(1-pyrene)propane (BPP) is 100 percent at much milder conditions of 365°C and time of 31 minutes. PPN is also found more reactive than diphenylpropane under similar reaction conditions. The pyrolysis of 1,3-bis(1-pyrene)propane (BPP) is an example of a residue molecule converting to other residue molecules after thermal cleavage of aliphatic linkage. The reaction products are produced by cleavage of C-C bond at the aryl-alkyl position or at other positions near the ring. The difference between the pyrolysis pathways of PPN and BPP is that the strong aryl-alkyl bond breaks only in the BPP pyrolysis. Various mechanisms are proposed to explain the cleavage of alkyl-aryl bond. Depending upon the cluster size of the aromatic rings attached by paraffin chain, the pyrolysis products of 1,3-diarylalkanes might be a gasoil or residue fraction molecule.

Hydroaromatics

The presence of the α-to-aromatic cycloparaffins in the NMR data of the pseudo-components points to the existence of the hydroaromatic and alkylhydroaromatic moieties in the oil. The kinetic data of these different model compounds indicate mole percent conversion of around 40 percent for 2-dodecyl-9,10-dihydrophenanthrene [9], 10 percent for 2-ethyltetralin [13] and around 1 percent for tetralin [14] at similar reaction severity. This indicates that polycyclic hydroaromatic moieties with long alkyl chains are more reactive. In the reaction network for 2-dodecyl-9,10-dihydrophenanthrene (DDPh), at the experimental severity, the dehydrogenation pathway is the major one with a

selectivity of 80-90 percent and only a small amount of other products are formed because of the side chain cleavage. But dehydrogenation of hydroaromatics would not lead to the conversion of residue fraction molecules like DDPh to lighter pseudo-components and thus this reaction would not contribute to residue conversion. In the pyrolysis pathways for 2-ethyltetralin (2ET), naphthalene along with dialin form the major products and the dehydrogenation of the naphthenic ring seems to be the prominent reaction. Thus, in the hydroaromatics pyrolysis, under the visbreaking conditions used, the major reaction pathway is the dehydrogenation of the naphthenic ring. The cleavage of the side chain at or near the ring is a minor pathway and does not contribute significantly to residue conversion to lighter pseudo-components.

Major Reactions during Visbreaking

From the pyrolysis studies of model compounds, it can be concluded that the polycyclic alkylaromatics are the most reactive species responsible for the residue conversion under visbreaking conditions, followed by the polycyclic cycloparaffins. The data in the work suggest that the cycloparaffin ring opening as well as the aromatic ring opening does not happen under the visbreaking conditions used. Also, aromatization of paraffin chains is not likely under the existing conditions. Among the cycloparaffins, only the hydroaromatics get dehydrogenated to aromatics. The main reaction pathway for the conversion of residue to distillates during visbreaking is that of the cleavage of side chains from polyaromatics.

Side Chain Cleavage

The average chain length in the residue fraction decreases in all feeds, with the exception of the American oil, during visbreaking. The maximum decrease in chain-length is observed in the Canadian and Middle East oil. With the decrease of the side chain length, the chain midsection carbon in residue also decreases and the percent decrease can be correlated to the percent residue conversion. The oil experiencing the maximum conversion has the maximum percent decrease of chain midsection carbon.

Cycloparaffin Dehydrogenation

The molar sum of aromatic and cycloparaffin carbon-types in the oils remains the same before and after cracking, with an error ranging from 3 to 9 percent. The conservation of moles of the aromatic and the naphthenic carbon-types in the oils before and after cracking implies that the rings do not get destroyed or formed; only the naphthenic rings are dehydrogenated to aromatics. Since the dehydrogenation is accompanied by the increase of boiling point and density, this does not lead to the formation of the lighter distillates.

Model Development

The main objective of this study is to develop a mathematical model, which is based on the principles of reaction chemistry and is able to predict the product yield of different fractions like gas, naphtha, gasoil, residue and coke after visbreaking of heavy oils at a single reaction severity. The six heavy oils chosen for the study are from different geographic regions of the world and are of different chemical nature. The basic assumption for the model is that at this severity, there are no secondary cracking reactions. It is also believed that most molecules in the feed pseudo-components do not react and for the most part, only one bond is broken for those that react.

Residue Conversion

The percent conversion during visbreaking from residue fraction ($524^{o}C+$) to distillates involves cracking to lighter products whose boiling point falls in the gasoil ($204-524^{o}C$), naphtha (IBP-$204^{o}C$) boiling range, or the gas range.

From the model compound studies, the most important pathway for the conversion of heavy oils during visbreaking is the side chain cleavage. The higher the alkyl substitution at the aromatic and possibly the naphthenic rings, the higher is the reactivity. Also the C-S bonds in the chains are weaker than other aliphatic bonds and are important cleavage sites. Thus, the residue conversion should be dependent upon the number of alkyl substituted aromatic and cycloparaffinic carbon-types and the sulfide 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 5 carbon atoms.

Previous work [20] suggested that side-chain cleavage of cycloparaffin species is minor due to the small ring cluster sizes (mostly 1 to 2 rings). As 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 calculation, the correlation with residue conversion was not as good.

Consequently, the contents of alkyl-substituted aromatic and sulphidic carbon and average chain lengths results were consolidated through the formulation of a Residue Reactivity Index (RRI) as

$$RRI = (A * B) + C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{...equation (1)}$$

where,

A= Content of alkyl substituted aromatic carbon (moles)
B= min (1, Alkyl chain length/5)
C= Content of α-to-sulfides (moles)

The residue weight percent conversion was found to correlate with RRI with a correlation coefficient (R^2) of 0.87 as shown in Figure 1. It is to be noted that the South American oil which shows the lowest residue conversion, has the least alkyl substitution of aromatics and the shortest chains. This appears to be the reason why there was low residue conversion despite a high aromatic content.
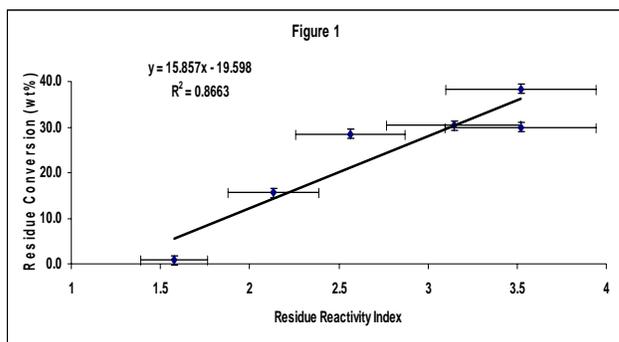
Figure 1: Residue conversion vs. Residue Reactivity Index

Coke Formation

Coke formation during visbreaking is measured by the toluene insolubles content of the visbroken product. The maximum visbreaking coke formation was observed in the South American oil, which has almost no residue conversion. 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 directly correlate with the contents of coke generated under the current conditions (correlation coefficient of 0.88) as seen in Figure 2. The contents of the total aromatic carbon do not correlate with the visbreaking coke as well. As 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.
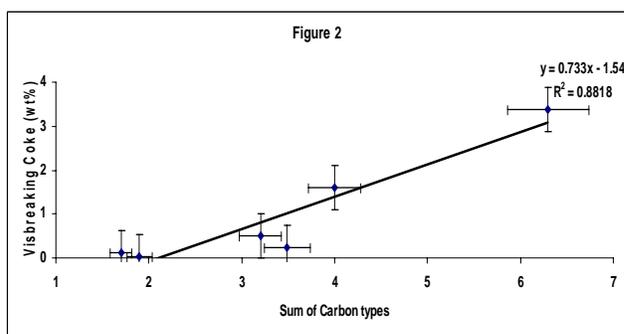

Figure 2: Visbreaking coke vs. Sum of Carbon types

Correlations for Gas and Naphtha Formation

In the previous work [1], reaction pathways for the formation of lighter products during visbreaking of Athabasca bitumen were proposed and validated using carbon balances. The same reaction pathways have been adapted for the visbreaking of these different oils and used to predict the gas phase and naphtha products. The reaction pathways indicate which carbon-types or groups of carbon-types in the feed are responsible for the production of methane, C2, C3+, naphtha aromatics, cycloparaffins and paraffins during the visbreaking reaction. The naphtha aromatics, paraffins and cycloparaffins combine together to form the total naphtha fraction. Throughout

the remaining section, different pseudo-components are referred to as GO, GOS, GOA, GOP, RS, RA, RP, and RAs, representing gasoil, gasoil saturates, gasoil aromatics, gasoil polars, residue saturates, residue aromatics, residue polars, and residue asphaltenes, respectively. The reaction pathway for methane conversion is described below.

Reaction Pathway for Methane Formation

The methyl cycloparaffins in all pseudo-components contribute to the formation of methane through cracking of the methyl group that forms methane. Since the aromatics in gasoil and residue saturates have cluster sizes of 1-2 rings, the C-C bond at the β position in the ethylaromatics crack to release the methyl group and form methane. However, in residue aromatics, polars and asphaltenes the aromatic cluster size is of the order of 3-4 ring and the alkyl-aryl bond breaks off preferentially in these polycyclic methylaromatics to release the methyl group that forms methane.

$$(A+B)_{GO}+(A+B)_{RS}+(A+C)_{RA+RP+RAs} => Methane…equation (2)$$

where A= Methylcycloparaffin carbon (moles), B=Ethylaromatic carbon (moles) and C=Methylaromatic carbon (moles)

In the overall model, the reaction pathways indicate the carbon-types that react to form gas and naphtha components and so were included as model parameters. The prediction of the amount of gas and naphtha components produced during visbreaking was achieved by building product correlations using the relevant carbon types of pseudo-components. As well, given the importance of aromatic cluster size on reactivity and reaction mechanism, aromatic cluster size was also included as a model parameter in the correlations. The feed carbon types responsible for the formation of gas and naphtha products and the aromatic cluster sizes were added together using relative weighting factors to form a weighted sum of model parameters. This weighted sum of model parameters was correlated with the moles of carbon-types produced in gas and naphtha fractions. The weighting factors were calculated based on Model rules.

Model Rules

The Model rules are formulated based on the knowledge gathered from the model compound pyrolysis chemistry and apply to all pseudo-components

Rule 1: The reactivity of alkyl substituted cycloparaffin CH is 60 percent of the reactivity of the alkyl substituted aromatic carbon. This is because the alkyl substituted aromatic carbon is the most reactive species in oil during visbreaking.

Rule 2: The propensity of gasoil to convert to gas and gasoil saturates to convert to naphtha is 10 percent of the propensity of the residue fraction (aromatics, polars and asphaltenes) to convert to gas and naphtha. This is because the composite gasoil and the gasoil saturates have lower aromatic content and being smaller, have smaller aromatic cluster size, both of which lead to lower reactivity.

Rule 3: The propensity of gasoil aromatics to convert to naphtha is 30 percent of the propensity of residue aromatics and polars to convert to naphtha. This is because the gasoil aromatics molecules are smaller and so have smaller aromatic cluster size leading to lower reactivity.

Rule 4: The propensity of residue saturates to convert to gas and naphtha is 30 percent of the propensity of residue aromatics, polars and asphaltenes to convert to gas and naphtha. This is because the residue saturates have lower aromatic content which makes them less reactive.

Rule 5: The propensity of residue asphaltenes to convert to gas is equal to the propensity of residue aromatics and polars to convert to gas. The propensity of residue asphaltenes to convert to naphtha is 50 percent of the propensity of residue aromatics and polars to convert to naphtha. This is because the asphaltenes with their shorter side chains are more likely to produce gas than naphtha.

Rule 6: The residual aromatics are the aromatic carbon-types other than the alkyl substituted aromatic carbon. The residual cycloparaffins are the cycloparaffinic carbon-types other than the cycloparaffinic alkyl substituted CH carbon. The paraffin chain ends are analogous to the residual paraffins. Thus the residual components are primarily the unreacted species during visbreaking. But they add to the aromatic or naphthenic or paraffinic nature of the reacting pseudo-components and thus play an important part in determining the quantity of naphtha aromatics, cycloparaffins and paraffins produced. Therefore, the residual aromatics, cycloparaffins and paraffins are considered twice as responsible as the alkyl substituted aromatic carbon for the production of naphtha aromatics, naphtha cycloparaffins and naphtha paraffins respectively.

Rule 7: The role of aromatic cluster size in determining the reactivity is less than that of alkyl aromatic substitution and the length of side chains. The effect of cluster size is thus considered as 15 percent of that of the aromatic alkyl substituted carbon in determining reactivity.

The calculation of weighting factors was done by attributing a base reactivity of 1 to a particular feed carbon-type and then calculating the other weighting factors using the model rules. The weighting factors signify the relative importance of different sources of a particular pseudo-component through a reaction pathway. Thus the product correlations were calculated for methane, C2, C3+, naphtha aromatics, naphtha cycloparaffins and naphtha paraffins. The product correlation for methane is described below.

Product Correlations – Methane Formation

The methane formed during visbreaking was correlated with the weighted sum of model parameters for all feeds using the following equation:

Weighted sum of model parameters = $b_1*C_{RAs} + b_2*C_{RP} + b_3*C_{RA} + b_4*A_{RAs} + b_5*A_{RP} + b_6*A_{RA} + b_7*B_{RS} + b_8*A_{RS} + b_9*B_{GO} + b_{10}*A_{GO}$……………………………… equation (8)

where A=Methylcycloparaffin carbon (moles), B=Ethylaromatic carbon (moles) and C=Methylaromatic carbon (moles)

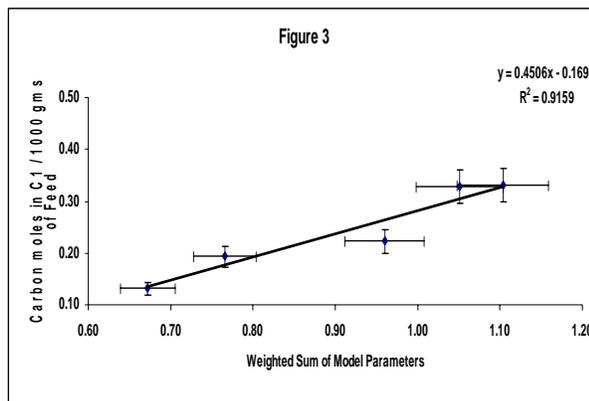Figure 3 shows the product correlation with a correlation coefficient of 0.92.

Figure 3: Carbon moles in methane

The final product yields were determined as follows. The residue fraction after visbreaking was calculated from the percentage residue conversion of the feed where the percentage residue conversion was determined using the Residue Reactivity Index of the feed. The sum of naphtha paraffins, cycloparaffins and aromatics produced during visbreaking gave the total naphtha produced. This was added to the quantity of feed naphtha to give the total product naphtha yield. The sum of methane, C2 and C3+ gave the total product gas yield. Finally, the gasoil product was calculated by balance.

Model Validation

The model was validated by removing one oil dataset, re-estimating the correlation equations and then predicting the product yields and calculating the percentage difference between the measured and predicted values. This process was repeated for three of the oils; the results for the Middle East oil are shown in Table 1. The percentage difference between the predicted and measured values is very high in visbreaking coke due to the very small amount of visbreaking coke that was formed.

	Middle East Oil		
Yield (wt%)	Experimental	Predicted	Difference%
Gas	0.8	0.7	5.6
Naphtha	14.5	14.4	0.6
Gasoil	56.1	56.2	0.2
Residue	28.6	28.7	0.1
Feed CCR	8.61	9.39	9.0
Vis. Coke	0.50	0.87	72.6

Table 1: Model validation

Conclusion

This work presents a mathematical model of visbreaking using nuclear magnetic resonance (NMR) – determined carbon-types present in feed oil. The model predicts residue conversion, coke formation and product yields. Since it has been built using six heavy oils from different parts of the world, it is expected to be robust enough to predict the visbreaking behavior of many different types of oil.

The model input data included carbon type content results for six heavy oils from an extensive type of NMR analysis carried out at the National Centre for Upgrading Technology, Devon, Alberta. This new information has helped to provide a much deeper insight into the chemistry of heavy oils during visbreaking and has assisted with the selection of model compounds that closely resemble different pseudo-components of these heavy oils. The pyrolysis pathways, the reaction mechanisms and the kinetic information of these model compounds available in literature has helped to identify the carbon-types and the reactions that influence visbreaking the most. In the earlier work [1], visbreaking reaction pathways for Athabasca bitumen were proposed. These pathways have been improved and adapted to the NMR information from different oils. These pathways indicate the carbon-types in feed oil that act as sources for the production of new carbon-types during visbreaking. Through the use of feed-independent model rules, weighting-factors were developed, and then used to calculate different weighted sum of model parameters in these oils. These weighted sums of model parameters are analogous to the pool of reactants and have been used to correlate percentage residue conversion, visbreaking coke-make and the production of lighter products, gas and naphtha, during visbreaking. From its ability to predict the visbreaking behavior of six different global oils, the model offers improved knowledge about the chemical reactivity of petroleum oils. It is found that the percentage conversion of heavy oil residue during visbreaking is dependent on the alkyl substituted aromatic carbon, alkyl chain length and the α-to-sulphides content in the feed residue fraction. So the reactivity of an oil depends upon the number of side chains attached to residue aromatic rings and the length of these side chains. The visbreaking coke is directly dependent upon the quantity of the aromatic bridges and aromatic CH carbon-types in the residue asphaltenes fraction of the feed. The gas and naphtha is produced due to the cleavage of side chains on the aromatic and cycloparaffinic rings in gasoil and residue fraction: the side chains crack to produce smaller molecules that constitute gas and naphtha.

The use of reaction pathways and feed-independent model rules make this model rule-based. Earlier models used feed-specific kinetic parameters to predict visbreaking product yields and these kinetic parameters were calculated based on visbreaking pilot plant runs or lab scale pyrolysis experiments. The present model only uses the NMR carbon-type and elemental analyses of distillation and SARA feed fractions to predict its visbreaking product yields. Along with the prediction of visbreaking behavior of other oils, the model was successful in predicting the residue conversion, coke yield and other product yields for a unconventional oil like the South American oil, which unexpectedly showed practically no residue conversion during mild thermal cracking. In being able to explain this phenomenon, the model furthers the understanding of the chemistry of such oils containing polycyclic aromatic species that have short alkyl-chains, and their behavior in upgrading plants and refineries.

Acknowledgement

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