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Mathematical Modeling of Thermal Conversion of Athabasca Bitumen

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Abstract

Modeling of a thermal cracking process involves establishing a set of kinetic reactions that transform the feed into products. In a typical feed, there exists a large number of real components. Thus, an exact feed composition is not known. The most common method to overcome this difficulty is to define pseudo-components based on one or more physical properties such as boiling point or molecular weight.

In this work, we propose a set of model thermal cracking reactions based on nuclear magnetic resonance (NMR) data. NMR carbon type analysis improves the characterization of the feed and products by providing the contents of different carbon species (carbon bonds). This additional information enables a more descriptive and fundamental set of reactions to be developed for the model. The reactions chosen describe the types of carbon bonds that break and form in the feedstock under visbreaking conditions. The set of reactions is the centre of the pseudo-component model.

Introduction

Visbreaking is a thermal cracking process that has existed for many decades. It is a relatively mild process used primarily to reduce the viscosity of the heavy ends of crude oil feedstocks that results in low conversion of heavy-end material. For example, typically there is < 30 wt % conversion of residue with boiling points (BP) > 524ºC to lower-boiling components. Visbreaking is widely used in Europe and Asia due to the properties of available feedstocks and demand for heavier products such as fuel oil. In Alberta, an increasing proportion of the oil produced is extra heavy (i.e. Athabasca bitumen). Consequently, higher severity processes such as coking and residue hydrocracking are needed to convert 60 wt % or more of the residue to lighter products suitable for transportation fuels. However, there has been some interest in visbreaking as a field upgrading process to reduce the need for diluent to meet pipeline specifications for bitumen and heavy oil transportation.

Despite visbreaking being a relatively simple process, modeling of the thermal cracking reactions that result in product formation poses many challenges. The greatest difficulty is to find a suitable method to describe the feedstock and product molecules. For the lightest components of crude oils (i.e. naphtha, BP < 204ºC), there are over a thousand molecular species that can be identified and quantified. However, for fractions with boiling points > 204ºC, virtually every molecule is different. Thus, the challenge is to lump the molecules into a manageable number of groups yet be able to retain enough chemical sensitivity so as to be able to develop fundamental correlations.

The most common method to characterize a feedstock is to define pseudo-component lumps based on physical properties like molecular weight or boiling point. However, as these

properties provide no specific information of the relative chemical reactivity of the lumps, the kinetic parameters determined are empirical and need to be adjusted for each different feedstock.

Recently, nuclear magnetic resonance (NMR) spectroscopy has been used for structural analyses of petroleum fractions. Ali et al.[1] used NMR data to estimate average molecular structures of Kuwaiti vacuum gas oil. Carbon type analysis using ^{13}C and ^{1}H NMR spectroscopy has proven useful for identifying the chemical structural features in petroleum fractions including residue components that are important during thermal processing. For example, the quantities of carbon types were used to assess the changes in product quality as residue was recycled under coking conditions by Japanwala et al[2]. Similarly, Rahmani et al.[3] used the results of carbon type analyses and sulphide content measurements to determine the dependence of coking kinetics on the chemical structures of asphaltenes. Finally, Sheremata et al.[4] used carbon type analyses results to construct molecular representations of the components in Athabasca bitumen asphaltenes. The current project focuses on a new application for carbon type analyses where the data will be used to develop a mathematical model of the thermal reactions that occur during visbreaking. In this paper, the model approach and proposed chemical reactions are described.

Background

Previously, some visbreaking process models have been developed. In the models proposed by Shu and Venkatesen[5] and Krishna et al.[6], visbreaking was described with 2 pseudo-components, a feed and a product. This approach only required one overall reaction, and the reaction predicted how much of the feed was converted into product. The model proposed by Shu and Venkatesan[5] was based on Cold Lake Bitumen while the model proposed by Krishna et al.[6] used Agjahari long residue as its feedstock. Each feedstock had its own set of pre-exponential factors and activation energies, illustrating that the fit of this type of model was feed-dependant. More recently, Singh et al.[7] proposed a model that included 1 pseudo-component for the feed and 5 product pseudo-components that were based on distillate fractions and a gas phase. Four different feedstocks were used, but each feedstock had to have its own set of estimated kinetic parameters. Again, the predictive ability of the model was limited to the feedstock used to validate the model.

New Pseudo-Component Definition

In the current work, the objective is to develop a model that will be predictive for many petroleum feedstocks. Consequently, pseudo-components were chosen with consideration of chemical reactivity, rather than being based solely on physical properties. Before analyses, the feedstock and liquid products were fractionated. Firstly, fractionation was based on boiling point: product gas; initial boiling point (IBP) to 204°C called naphtha; 204°C to 524°C called gas oil; and +524°C called residue. Secondly, the gas oil and residue fractions were separated by polarity using the SARA (saturates, aromatics-resins(polars), and asphaltenes) method: the gas oils were separated into 2 fractions (saturates and aromatics+polars); and the residues were separated into 3 fractions (saturates, aromatics+polars, and asphaltenes). This resulted in a set of 5 pseudo-components for the feed, as the

naphtha content of the feedstock was too low to be able to analyze, and 7 pseudo-components for the products. The list of the pseudo-components for the model is given in Table 1. The analyses of the liquid and solid fractions included density, boiling point distribution, molecular weight, elemental, and carbon type. The carbon types quantified using NMR spectroscopy are shown in Figure 1. For the gas samples, the hydrocarbon content information from the refinery gas analyses were also distributed according to the carbon types shown in Figure 1.

This definition for pseudo-components and particularly, the carbon type information should enable the model to be predictive for different petroleum feedstocks. The types of carbon will not change from feedstock to feedstock, only the relative quantities will vary. For example, a heavier feed will have more of the gas oil and residue fractions, and possibly consist of more of the aromatic carbon types. A lighter feed will have more naphtha and gas oil, and possibly consist of more of the non-aromatic (aliphatic) carbon types.

Experimental Data

Fraction Preparation

The feedstock chosen for this study was Athabasca bitumen from the Underground Test Facility (UTF), an extra-heavy oil with a high sulfur content. After processing, the feed and total liquid products (TLPs) were distilled into the cuts shown in Table 1 using the American Society for Testing and Materials[8] (ASTM) D1160 method.

Asphaltenes were precipitated from the D1160 vacuum residues (BP > 524ºC) with pentane using a single treatment of the procedure outlined in Peramanu et al[9]. This method includes adding 40-volumes of pentane, sonicating in a bath sonicator for 45 minutes, leaving the mixture to rest overnight at room temperature, then sonicating for an additional 30 minutes before filtering and, washing with pentane until the eluent is colorless. The solid (asphaltenes) were dried in a vacuum oven at 45ºC until constant weight was obtained. The pentane solvent was removed from the eluent (maltenes) by rotoevaporation.

The gas oil and the residue maltenes were separated into saturates and aromatics+polars fractions using a modification of the clay-gel adsorption chromatography method described in Peramanu et al[9]. After collection of the saturates sample using pentane, the polar fraction was adsorbed to the upper attapulgus clay while the aromatics fraction adsorbed to the lower silica gel column. The columns were separated and the aromatics eluted from the silica gel by washing with 2.5 volumes of methylene chloride. The polars were removed from the clay by washing successively with 3.3 volumes of methylene chloride, 3.3 volumes of methanol:methylene chloride (60:40) and finally 1.7 volumes of methanol. The aromatic and polar fractions were pooled, rotoevaporated to constant volume, then dried in a 45°C vacuum oven until constant weight was obtained. The pseudo-component mass fractions in the feed are given in Table 2.

Fraction Characterization

Gas and Naphtha Component Analysis

Refinery gas analysis was run on the gas product on either a Refinery Gas Analyzer (MTI) or Agilent Technologies 3000A gas chromatography (GC) instrument. PIONA (paraffin, isoparaffin, olefin, naphthene, and aromatic) analyses of the naphtha products were performed on an Agilent Technologies 6890 GC instrument.

Density Measurements

The densities of the naphtha and gas oil samples were measured using the ASTM D4052 method on a Mettler Toledo Density meter (DE45). The densities of the residue samples were measured on a helium pycnometer (Micromeritics 1320) using the ASTM method D2638 for saturates and asphaltenes, and D2320 for aromatics+polars.

High Temperature Simulated Distillation

High temperature simulated distillation (HTSD) (ASTM D6352-02) was performed on an Agilent Technologies 5890 GC instrument using Analytical Control software.

Elemental Analyses

Sulphur contents of naphtha were measured using x-ray fluorescence (ASTM D4294) on a Horiba XR Fluorometer (SLFA-1800). The sulphur contents of the gas oil saturates were measured by GC (Agilent Technologies 6890) using sulphur chemiluminescence detection (ASTM D5623). The sulphur contents of all other samples were measured using a Leco SC 432 analyzer where ASTM D1552 was used for the aromatics+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 contents of the saturates were 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+polars, and ASTM D5373 for the asphaltenes. The carbon and hydrogen contents of the naphtha were measured on the Leco 1000 Analyzer using the ASTM D5291 procedure.

Average Molecular Weight Measurements

Average molecular weights for all samples except naphtha were measured by vapor pressure osmometry using o-dichlorobenzene at 120ºC, as described in Peramanu et al[9]. The average molecular weights of naphtha were measured by freezing point depression using a Wide-Range Cryette (WR™).

Nuclear Magnetic Resonance Spectroscopy

NMR analyses were performed at room temperature $(19 \pm 1ºC)$ on a Varian Unity Inova 600 NMR spectrometer, operating at 599.733 MHz for proton and 150.817 MHz for carbon. For proton, 20 mg quantities were dissolved in 700 μL deutero-chloroform. For carbon, 50 mg quantities of asphaltenes were dissolved in 700 μL deutero-chloroform while 100 mg or μL quantities of the other samples were dissolved in 600 μL deutero-chloroform. Both proton and carbon spectra were run using a Varian 5 mm broadband $^{13}C\{^{1}H\}$ probe.

The quantitative carbon spectra were acquired using an acquisition time of 1.0 s and a sweep width of 36003.6 Hz. For residue samples, a flip angle of 35º (4.6 μs) and a relaxation delay of 5s were used. For naphtha and gas oil samples, a flip angle of 26.4º (3.4 μs) and a relaxation delay of 10 s were used. Reverse-gated waltz proton decoupling was used to avoid nuclear Overhauser effect enhancements of the protonated carbon signals. The spectra were the result of 2048 scans. Line broadening of 5 Hz for the naphtha, 10 Hz for the gas oil and 15 Hz for the residue samples was used to improve the signal-to-noise ratio of the spectra. The spectra were referenced to the deutero-chloroform resonance being set to 77 ppm.

The quantitative proton spectra were acquired using an acquisition time of 3 s and a sweep width of 20000 Hz. A flip angle of 30.6º (3.3 μs) and no relaxation delay were used. The spectra were the result of 128 scans. Line broadening of 0.33 Hz was used to improve the signal-to-noise ratio of the spectra. The spectra were referenced to the deutero-chloroform resonance being set to 7.24 ppm. Spectra were processed using a procedure based on that described in Japanwala et al[2].

Visbreaker Operating Conditions

The unit, operating as a soaker-type visbreaker, performed a total of nine runs at five temperatures, two feed flow rates and two retention times. The experimental conditions for each run are listed in Table 3. The reactor pressure was set at 1 MPa.

Model Approach and Discussion

Chemical Reaction Definition

Figure 1 shows that NMR carbon type analysis has been developed to quantify all carbon types in petroleum feeds and products. As these results describe the carbon bonds in the feed and products, changes in distribution of carbon types in the TLP relative to the feed reflect the process chemistry. Modeling this information will reveal the relative importance of the different reactions that have taken place in these complex systems.

For the mild thermal conditions used during visbreaking, it was assumed that the products did not undergo further reaction. In Table 3, the contents of toluene insolubles (TIs) are given. By definition, coke is insoluble in toluene, so an increase in the TI content would indicate coke formation. As coke formation is evidence of further product reaction (i.e. polymerization), the results in Table 3 suggest that six of the runs will meet this assumption while three runs (5, 8 and 9) may not.

Table 4 shows the cleavage reaction products expected from alkyl sulphide species in the bitumen. For carbon-carbon bond cleavage, Gary and Handwerk[10] suggested that the principal reactions that take place under visbreaking conditions involve substituted aromatic and cycloparaffin rings of varying cluster sizes (Table 5). Also included was a reaction involving 2-ethyltetralin to describe cycloparaffin dehydrogenation. This hydroaromatic was chosen because a cycloparaffin ring is more likely to dehydrogenate when it is part of a poly-ring system with aromatics. A cycloparaffin ring by itself is less likely to dehydrogenate. Aromatics and cycloparaffins with long side chains were chosen to allow for the greatest variety of possible products. All of the model reactions chosen can be approximated as first order reactions.

Examples of how the reactions shown may be monitored are the following. A simple reaction is the dehydrogenation of

cycloparaffin rings to form aromatic rings: the decrease in cycloparaffinic carbon content (Figure 1) in the TLP relative to the feed is equal to the increase in aromatic carbon content in the TLP relative to the feed. As well, dehydrogenation of cycloparaffin rings in the feed is thought to be primarily responsible for H_2 formation in the product gas.

For methyl species, the total of aromatic, cycloparaffinic and branched-alkane methyl carbons in the feed should be equivalent to the total of methane, aromatic, cycloparaffinic and branched-alkane methyl carbons found in the TLP.

The cleavage of alkyl sulphide bonds generates olefins and hydrogen sulphide. Consequently, formation of hydrogen sulphide gas and a decrease in sulphur content in the TLP relative to the feed reflects this chemistry. The olefin formation would also result in an increase in olefinic carbon content in the TLP relative to the feed. However, formation of olefinic carbon can be due to several other mechanisms as shown in Table 5. The relative contributions of the different reactions to olefinic carbon formation will be determined by the model.

Model Formulation

The final form of the mathematical model will be such that it can be used as a tool to predict visbreaking yields based on carbon type analysis data for any given feedstock. For alkyl sulphide conversion, the analytical data contains the necessary information to estimate conversion without requiring additional kinetic information. For the model reactions described in Table 5, kinetic information is available from the literature so conversion and product distributions can be estimated. Because the pseudo-components are based on carbon type (carbon bond) lumps, the kinetics will be developed on fundamental reactivity principles and so will be more consistent than models based on empirical information.

Conclusion and Future Work

Carbon type analyses performed using NMR spectroscopy has been developed to determine the distribution of carbon types present in petroleum liquid and chloroform-soluble solid fractions. This new information is currently being used to develop a fundamental model for predicting the product composition and yields generated during visbreaking. More specifically, the balances on various carbon types that appear and disappear during thermal cracking will be used for final validation. Future work will focus on testing the applicability of the visbreaking model with different feedstocks. Further work would expand the model to include more severe process conditions such as residue hydrocracking and coking.

Acknowledgement

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Separation by:	Fractions			
Boiling Point	Gas	Naphtha (N) (IBP-204°C)	Gas Oil (204°C - 524°C)	Residue (+524°C)
Polarity	-	-	Saturates (GO-S) Aromatics+Polars (GO-A+P)	Saturates (R-S) Aromatics+Polars (R-A+P) Asphaltenes (R-As)

Table 1: List of Model Pseudo-Components

Pseudo-Component	Feed (wt.%)
Gas	0
N	0
GO-S	0.186
GO-A+P	0.276
R-S	0.0307
R-A+P	0.338
R-As	0.170

Table 2: Mass Fractions of Pseudo-Components in Feed

Run	Temperature (°C)	Flow Rate (kg/h)	Retention Time (min)	Toluene Insolubles (wt %)
Feed	-	-	-	0.38
1	390	2	30	0.49
2	405	2	30	0.54
3	405	3	20	0.55
4	420	3	20	0.64
5	420	2	30	2.26
6	415	2	30	0.90
7	415	3	20	0.33
8	430	3	20	2.46
9	430	2	30	3.75

Table 3: Experimental Conditions and Toluene Insolubles Content
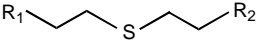
Compound	Major Products
Alkyl Sulphides $R_1 \diagup\!\!\!\diagdown S \diagdown\!\!\!\diagup R_2$	Hydrogen Sulphide H_2S 1-Olefin species $R_1 \diagup\!\!\!\diagdown$ + $\diagdown\!\!\!\diagup R_2$

Table 4: Model Reactions – Carbon-Sulphur Bond Breakage
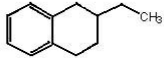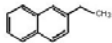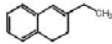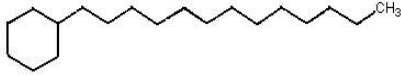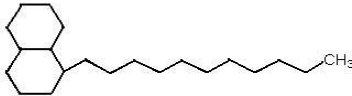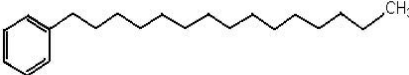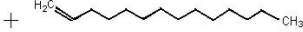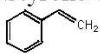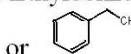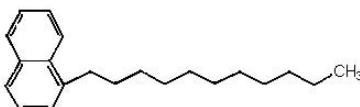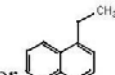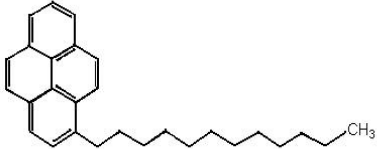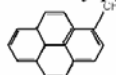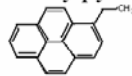
Compound	Major Products	Reference
1) 2-Ethyltetralin	Naphthalene 2-Ethylnaphthalene Dialin 2-Ethyldialin	11
2) Tridecylcyclohexane	Cyclohexane + Tridecene Methylenecyclohexane + Dodecane Methylcyclohexane + Dodecene	11
3) 1-Undecyldecalin	Octahydronaphthalene + Undecane 1-Methylenedecalin + Decane Decalin + Undecene	12
4) Pentadecylbenzene	Toluene + Tetradecene Styrene or Ethylbenzene + Tridecane	13
5) 1-Undecylnaphthalene	1-Methylnaphthalene + Decene 1-Vinylnaphthalene or 1-Ethylnaphthalene + Nonane	14
6) 1-Dodecylpyrene	1-Methylpyrene + Undecene 1-Ethylpyrene + Decane Pyrene + Dodecane	15

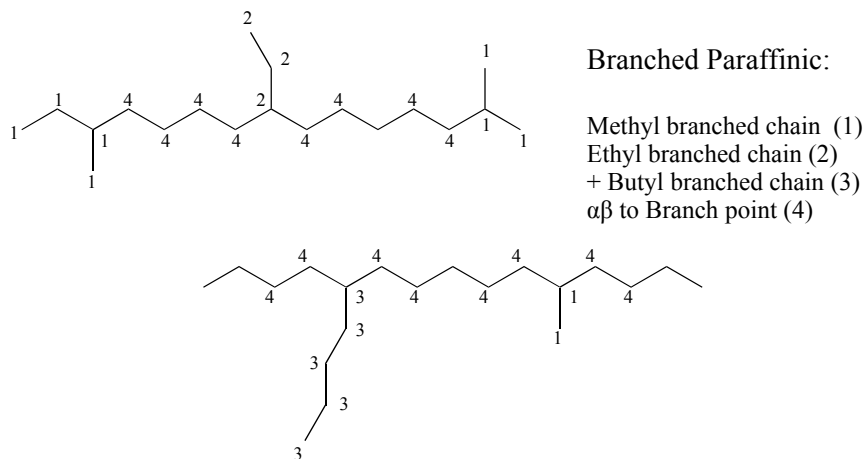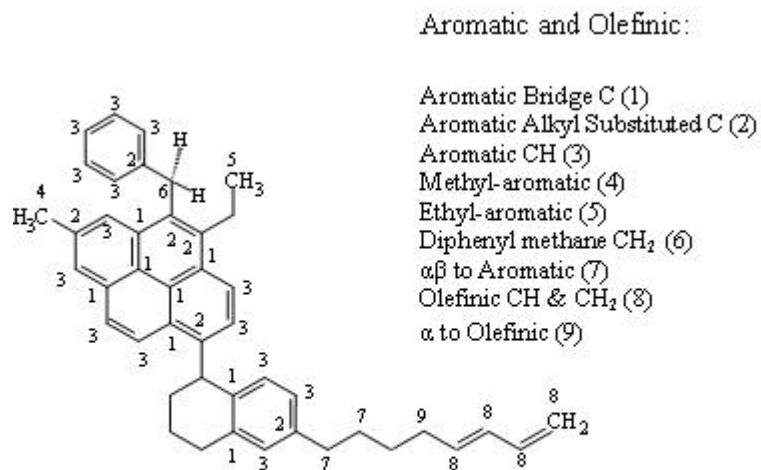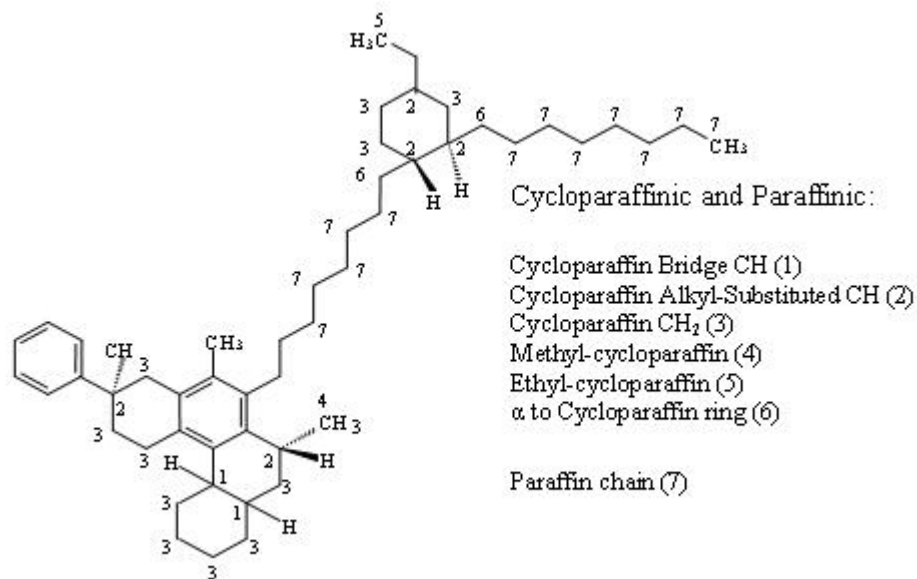Table 5: Model Reactions – Carbon-Carbon Bond Breakage

Figure 1: Molecular structures that illustrate the carbon types quantified using ^{13}C and ^{1}H NMR spectroscopy