Petroleomics Applications of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: Crude Oil and Bitumen Analysis

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PETROLEOMICS APPLICATIONS OF FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY: CRUDE OIL AND BITUMEN ANALYSIS

By

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ABSTRACT

The ultra-high mass resolving power and high mass accuracy of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) have been shown to be well suited for the characterization of highly complex mixtures. Petroleum mixtures, arguably the most complex on the planet, have been extensively characterized by FT-ICR MS. This new field of “Petroleomics”, spearheaded by the Ion Cyclotron Resonance group at the National High Magnetic Field Laboratory, presents the opportunity to address both fundamental aspects of petroleum chemistry as well as costly upstream and downstream processing issues.

Field desorption ionization (FD) provides access to non-polar hydrocarbons and low-polarity sulfur constituents of petroleum not accessible by the more common electrospray ionization (ESI). Chapter 2 describes the complete automation of the NHMFL 9.4 Tesla FD FT-ICR mass spectrometer and the benefits thereof. Automation allows ensemble averaging for increased dynamic range, mass accuracy, S/N and unattended sample analysis.

The decrease in light “sweet” crude oils has led to the use of heavier, more heteroatom rich feedstocks for the production of petroleum products. The oil sands bitumen deposits in Alberta, Canada represent a substantial reserve of recoverable crude oil. However, the high viscosity and high heteroatom content present production issues of this heavy oil. In particular, the high acid content (termed naphthenic acids) of Athabasca bitumen results in reduced market price due to the possibility of acid induced refinery corrosion (naphthenic acid corrosion). In Chapter 3 the characterization of organic acids in Athabasca bitumen and its heavy vacuum gas oil (HVGO) by negative-ion ESI FT-ICR MS are described. Advantages of acid isolation by ion-exchange chromatography are also discussed.
In Chapter 4, eight distillation cuts of an Athabasca bitumen HVGO are characterized by negative-ion and positive-ion ESI, as well as automated LIFDI (discussed in Chapter 2) FT-ICR MS to investigate the evolution of acidic, basic and non-polar species under standard distillation conditions. All methods reveal an increase in double-bond equivalents (DBE, the number of rings plus double bonds) and carbon number with increased distillation temperature range. Estimation of carbon number and DBE distributions for individual distillation cuts from the high-resolution feed HVGO mass spectrum is discussed.

The vacuum distillation tower has been shown to be highly susceptible to naphthenic acid corrosion, especially in the HVGO distillation temperature range of 220-400 °C. However, the thermal stability of petroleum acids in the temperature range is unknown. In Chapter 5, thermal treatment products of Athabasca bitumen are characterized by negative-ion ESI FT-ICR MS. Low-molecular weight organic acids are identified in the reactor inert sweep gas at higher treatment temperatures, suggesting boil-off.

Self-association of petroleum molecules, such as asphaltenes, in solution is well known. Chapter 6 describes the self-association of organic acids in the gas phase for crude oil and bitumen characterized by low-resolution and high-resolution mass spectrometry. Multimer formation is found to be concentration, boiling point and chemical functionality dependent. The results discussed in Chapter 6 suggest molecular weight determination for petroleum products by mass spectrometry should be scrutinized closely.

Asphaltenes are the most aromatic and most polar constituents of crude oil and are typically defined by their solubility. They are typically stable under reservoir conditions, but environmental changes in the production may disrupt their stability and cause costly deposition and precipitation problems. Chemical inhibitors are often added to the well
to prevent asphaltene deposition. Chapter 7 discusses asphaltene inhibitor specificity related to detailed polar chemical composition for two geographically distinct crude oils derived from negative-ion and positive-ion ESI FT-ICR MS.

Crude oils are commonly separated by their solubility in different solvents to simplify their characterization. Chapter 8 discusses the advantages and disadvantages of the saturate/aromatic/resin/asphaltene (SARA) chromatographic method for crude oil separation. FD and negative/positive-ion FT-ICR MS show compositional bleed between SARA fractions. Fractionation does facilitate identification of species not observed in the parent crude oil.

The appendices include the description of three unpublished collaborations related to bitumen extraction and production. Appendix A discusses the effect of acidic species in Athabasca bitumen on oil sand ore processability. Bitumen recovered from “good” ore and “bad” ore are analyzed and the results suggest naphthenic acid composition does not effect processability. Appendix B discusses the effect of acid species in Athabasca bitumen on emulsion formation. A bitumen sample and the bitumen component of a water/oil emulsion are found to be similar. However, the water soluble organic acids may contribute to emulsion formation. Appendix C discusses issues related to the handling of petroleum samples prior to ESI mass spectral analysis. The results suggest minor compositional changes under certain storage conditions.
CHAPTER 1.

INTRODUCTION

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Cyclotron Motion

Ion cyclotron motion results from the interaction of an ion with a magnetic field. Specifically, an ion moving in the presence of a spatially uniform magnetic field is bent into a circle by a Lorentz force (FL) that is perpendicular to the ion motion and the magnetic field, as shown by Eq. (1.1) (S.I. units),

\[ \mathbf{F}_L = \text{mass} \times \text{acceleration} = q \mathbf{v} \times \mathbf{B} \]  

in which \( q \) and \( \mathbf{v} \) are ionic charge and velocity and \( \mathbf{B} \) is magnetic field. If the ion velocity in the \( xy \) plane (i.e. perpendicular to \( \mathbf{B} \)) is denoted as \( v_{xy} = \sqrt{v_x^2 + v_y^2} \) and because angular acceleration, \( |dv/dt| = v_{xy}^2/r \), Eq. (1.1) becomes Eq. (1.2),

\[ qv_{xy}B_0 = \frac{mv_{xy}^2}{r} \]

where \( m \) is the ionic mass and \( r \) is the ion cyclotron orbital radius. Substitution for angular velocity, \( \omega = \frac{v_{xy}}{r} \) (in radians/second), yields Eq. (1.3) (S.I. units),

\[ \omega_c = \frac{qB_0}{m} \]  

(1.3)
where $\omega_c$ is the “unperturbed” ion cyclotron frequency, and similarly Eq. (1.4),

$$v_c = \frac{\omega_c}{2\pi} = \frac{1.535611 \times 10^7 B_0}{m/z}$$

(1.4)

where $v_c$ is the cyclotron frequency in Hertz, $B_0$ is the magnetic field in Tesla, $m$ is the ion mass in Daltons and $z$ in multiples of elementary charge.

**Excitation and Detection for FT-ICR Mass Spectrometry**

Ion cyclotron motion alone is not useful, as the cyclotron radius is too small to be detected and ions are not coherent in the ion trap. Thus, ions are excited by application of a spatially uniform rf electric field that oscillates at or near their cyclotron frequency. Ions with the same cyclotron frequency as the applied oscillating electric field absorb power from that field, which accelerates ions coherently to a larger (and thus detectable) orbital radius. An rf frequency sweep (chirp) excitation is used to excite a collection of ions with a range of m/z values. The ion cyclotron frequency for ions of typical molecules ranges from a few kHz to a few MHz. Therefore, commercially available electronics are used to generate excitation waveforms and measure induced ion current.

The coherent ion packet induces a charge on two opposed conductive detection plates. A current is induced in the plates, which is proportional to the ICR signal. Thus, a wide m/z range of ions can be detected simultaneously. The detected signal is sent to the data station where the time domain data is converted to a frequency spectrum via fast Fourier transform.
Mass Calibration

A small electrostatic trapping potential is applied in the ICR cell to limit ejection of ions along the z-axis (i.e. along or opposed to the magnetic field direction). However, this potential induces a radial force that is opposite to the Lorentz force from the applied magnetic field. A frequency to m/z calibration is used to correct for the electrostatic trapping potential. The most widely used form is shown in Equation 1.5,

\[
\frac{m}{z} = \frac{A}{v_+} + \frac{B}{v_+^2}
\]  

(1.5)

where A and B are constants found by fitting a set of ICR mass spectral peak frequencies for ions of at least two known m/z values to this equation.\(^1\),\(^2\) Thus, calibration of the mass spectrum by this method (i.e. internal calibration) yields excellent mass accuracy (< 1 ppm) because the analyte and calibrant ions experience the same electric and magnetic fields throughout the experiment.\(^3\)

Petroleomics

Petroleomics is the prediction of properties and behavior based on the composition of crude oil (and other petroleum derived samples).\(^4\),\(^5\) The composition of petroleum products determines both the upstream (production) and downstream (processing) behavior; not to mention product yields and quality, which all affect the economic value of the crude oil. Heteroatom composition (nitrogen, sulfur and oxygen) plays a large role in a number of production (solid deposition and flocculation) and processing (refinery corrosion and catalyst deactivation) problems. In addition, compositional information is paramount for the design and
selection of additives for the prevention of asphaltene flocculation, asphaltene deposition and the formation of other costly solid deposits in pipelines and processing equipment. Moreover, the environmental impact of heteroatomic compounds containing nitrogen and sulfur, namely the production of NO\textsubscript{x} and SO\textsubscript{x} emissions upon combustion, is under increased scrutiny by the Environmental Protection Agency. The decrease in light “sweet” crude oils (typically rich in low-boiling constituents) increases the interest in heavy “sour” crude oils, which are more complex and contain more aromatic, heteroatom containing constituents (nitrogen, sulfur and oxygen) with higher boiling point and are more prone to the costly problems mentioned above.

The importance of molecular-based descriptions to predict the behavior of complex petroleum samples is not a new idea. In the 1990’s, Quann and Jaffe stressed the importance of molecular-based models and developed structure-oriented lumping to deal with the immense complexity of petroleum samples, in light of the limitations of available analytical techniques.\textsuperscript{6} In addition, Boduszynski et. al. published a series of papers, beginning in the mid-1980’s, with comprehensive characterization of heavy petroleum by a variety of analytical methods.\textsuperscript{7-10} However, the time needed for these extensive studies makes the characterization of all petroleum samples of interest cumbersome.

The advent of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) in the 1970’s offered a new tool for the characterization of the “petroleome”\textsuperscript{11,12} The ultra-high mass resolving power and high mass accuracy of FT-ICR MS allow the assignment of unique elemental formulas to each peak in a mass spectrum. Thus, FT-ICR MS is, in principle, well suited to characterize complex mixtures such as petroleum.\textsuperscript{3-5} However, the power of FT-ICR MS for the analysis of petroleum samples was not realized until the mid-1990’s.\textsuperscript{13-17} In the past ten years, advances in FT-ICR instrumentation, ionization methods
and computer technology have solidified FT-ICR MS as a powerful tool in the analysis of the petroleome.\textsuperscript{4, 5}

**Need for Ultra-high Mass Resolving Power and High Mass Accuracy**

Petroleum crude oil is one of the most complex organic mixtures in the world. FT-ICR MS has identified over 11,000 peaks in a single positive-ion electrospray ionization (ESI) mass spectrum, as seen in Figure 1.1. The inset in Figure 1.1 shows the complexity at a single nominal mass; 25 peaks in a mass range of less than 1 mass unit.

![Figure 1.1: Broadband positive-ion ESI FT-ICR mass spectrum of a South American heavy crude oil illustrates the possible complexity of petroleum samples. Inset shows 25 unique peaks at a single nominal mass of m/z 588. Data kindly provided by Dr. Ryan P. Rodgers.](image)

South American Heavy Crude Oil  
9.4 T (+) ESI FT-ICR MS  
11,127 peaks >3σ baseline noise, 250-1000 Da

25 peaks at a single nominal mass

m/z: 225 375 525 675 825 975
Further, **Figure 1.2** shows a negative-ion ESI FT-ICR selective-ion accumulation mass spectrum at a nominal mass of 629 m/z for acidic asphaltenes with 55 individual peaks identified.

**54 Elemental Compositions at a Single Nominal Mass**

![Mass Spectrum](image)

Figure 1.2: Selective-ion negative-ion ESI FT-ICR mass spectrum of m/z 629 of asphaltenes from extra-heavy crude oil. 55 peaks and 54 elemental compositions unique to the asphaltene sample were identified at one nominal mass. Data kindly provided by Dr. Ryan P. Rodgers.

Most mass analyzers do not have a peak capacity (i.e. the spectral range divided by the typical peak width) high enough to resolve all of the peaks shown in Figure 1.2. The ultra-high mass resolving power (m/Δm_{50%} >350,000, where m is the ion mass and Δm_{50%} is the mass spectral full width at half-maximum height) of FT-ICR MS allows resolution of all 11,000 peaks in Figure 1.1 and ions with very similar masses. For example, the difference between the elemental compositions C₃ and S₁H₄, 3.4 mDa, an important split found in petroleum mass spectra. **Table 1.1** shows typical mass spacing differences (Δm) and the mass resolving...
power \((m/\Delta m)\) required for baseline resolution of typical doublets observed in petroleum FT-ICR mass spectra.

Table 1.1: Typical mass spacing differences observed in petroleum FT-ICR mass spectra and the required mass resolving power required for baseline resolution.

<table>
<thead>
<tr>
<th>Doublet</th>
<th>((\Delta m))</th>
<th>((m/\Delta m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_3) vs. (S_1H_4)</td>
<td>3.4 mDa</td>
<td>135 000</td>
</tr>
<tr>
<td>(C_2H_3) vs. (^{13}C_1N_1)</td>
<td>17.0 mDa</td>
<td>27 000</td>
</tr>
<tr>
<td>(C_1H_4) vs. (O_1)</td>
<td>36.4 mDa</td>
<td>13 000</td>
</tr>
<tr>
<td>(C_1) vs. (H_{12})</td>
<td>93.9 mDa</td>
<td>5 000</td>
</tr>
</tbody>
</table>

High mass resolving power alone does not make FT-ICR MS a powerful tool for molecular characterization of complex mixtures. The sub-ppm mass accuracy of FT-ICR MS allows assignment of unique elemental compositions \((C_{n}H_{m}N_{n}S_{s}O_{o})\) to peaks up to ~ 400 m/z. As discussed above, the application of a d.c. trapping potential affects the observed cyclotron frequency. Petrochemical samples present a convenient mode for internal calibration; homologous alkylation series. High abundance species with the same core structure, but differing in elemental composition by multiples of \(-\text{CH}_2\) groups, span most of the mass spectral range and are present in almost all samples. Therefore, the calibrant ions experience the same electric and magnetic fields of the analyte ions and sub-ppm mass accuracy over essentially the entire mass spectral range is achieved.

Mass accuracy for FT-ICR MS is highest at low d.c trapping potentials. Thus, there are few ions in the trap and signal to noise ratio \((S/N)\) is low. Ensemble averaging (50-300 averaged scans) is used to increase the \(S/N\) ratio for a greater dynamic range (ratio of strongest signal to weakest signal), accurate relative abundances and better mass measurement accuracy for low \(S/N\) peaks.
Kendrick Mass Sorting, Data Handling and Graphical Representation

As noted above, confident elemental compositions can only be made up to m/z ~400; but as Fig. 1.1 shows, FT-ICR mass spectra of petroleum samples can extend up to almost 1,000 Da. Homologous alkylation series are again exploited to aid in assignment of higher mass species. Mass spectra are converted from the IUPAC mass scale to the Kendrick mass scale so that the mass of CH$_2$ (IUPAC mass, 14.0156 Da) becomes exactly 14.0000. Equation 1.6 shows the formula for conversion of IUPAC mass to Kendrick mass.$^{19}$

$$\text{Kendrick Mass} = \text{IUPAC Mass} \times (14.0000/14.0156) \quad (1.6)$$

Compounds with the same core structure (N, S, O heteroatom composition and the same number of rings and/or double bonds), but different numbers of CH$_2$ groups now differ in Kendrick mass by multiples of 14.0000 and have the same Kendrick mass defect, as calculated by Equation 1.7.$^{19}$

$$\text{Kendrick mass defect (KMD)} =$$

$$(\text{nominal Kendrick mass} – \text{exact Kendrick mass}) \quad (1.7)$$

Identification of homologous series across the mass range are easily identified by their KMD, which is unique to each homologous series. Thus, it is possible to confidently assign molecular formulas to high-mass peaks by extrapolation from low-mass members of the same homologous series that have unambiguous elemental composition assignments.$^{20}$

For example, octanoic acid (C$_8$H$_{16}$O$_2$) has an IUPAC mass off 144.1150 Da. The Kendrick mass is thus:

$$(144.1150 \text{ Da} \times (14.0000/14.0156)) = \mathbf{143.9546 \text{ Da}}$$
Finally, the KMD is:

\[(144.0000 - 143.9546) = \mathbf{0.0454}\]

The same calculation for nonanoic acid (C\textsubscript{9}H\textsubscript{18}O\textsubscript{2}, IUPAC mass 158.1307 Da) yields a Kendrick mass of 157.9547 Da and a KMD of \mathbf{0.0453}. Thus, all saturated fatty acids will have a KMD of ~0.0454 and are easily identified and assigned.

The large amount of data from each FT-ICR MS experiment must be presented in an ordered, logical way. Visual inspection of the broadband mass spectrum only provides the mass distribution and illustrates the compositional complexity. Elemental composition assignment and Kendrick mass sorting yield three useful characteristics for petroleum: class (heteroatom content; N, S and O), type (hydrogen deficiency or the number of rings and/or double bonds) and carbon number distribution (number of CH\textsubscript{2} groups). Our laboratory has moved almost exclusively to class distribution graphs (heteroatom content) and color-coded isoabundance plots of double bond equivalents (DBE, the number of rings and or double bonds) versus number of carbons to simplify data interpretation.

The class distribution graph shows major differences in the relative abundance of heteroatom containing species (N, S and O). Figure 1.3 shows the class distribution for selected classes in an Arabian medium crude oil obtained from negative-ion ESI FT-ICR MS. Replicate experiments for co-added (10-200 experiments) electrospray, APPI and automated LIFDI FT-ICR mass spectra typically yield relative abundance errors between 3-8%. The error bars in Fig. 1.4 are +/- 5% of the class relative abundance. It is not easy to relate relative abundance in Fig. 1.3 to the actual abundance in the crude oil, due to differences in ionization efficiency and matrix effects. However, class distribution graphs show overall heteroatom distribution changes that can be analyzed in more depth by isoabundance contour plots of double bond equivalents versus the carbon number.
Assignment of elemental compositions also allows the calculation of hydrogen deficiency, or type, for each species identified. Double bond equivalents (DBE), or the number of rings and/or double bonds in the molecule, is an intuitive method for reporting the aromaticity. For a molecule with the general formula $\text{C}_c\text{H}_h\text{N}_n\text{S}_s\text{O}_o$, DBE is calculated by Equation 1.8.\textsuperscript{21}

$$\text{DBE} = c - \frac{h}{2} + \frac{n}{2} + 1$$

(1.8)

Aromatic and non-aromatic structures can now be easily identified by their DBE value.

Figure 1.3: Heteroatom class distribution (heteroatom content) for selected classes of an Arabian medium crude oil derived from negative-ion ESI FT-ICR MS. Class analysis highlights major differences of heteroatom containing species (N, S and O)
Broad trends for each class can be visualized by color-coded isoabundance plots of DBE versus the carbon number; as shown in Figure 1.4 for the N₁ class from the Arabian medium crude oil shown in Fig. 1.3. The x-axis is carbon number, which indicates the extent of alkylation, the y-axis indicates the aromaticity and the third dimension is the percent relative abundance represented by color. These images provide compact visualization for each class and easily demonstrate compositional differences.

N₁ Class: (-) ESI FT-ICR MS, Arabian Medium Crude Oil

Figure 1.4: Color-coded isoabundance contour for a plot of DBE versus the carbon number for the N₁ class of an Arabian medium crude oil derived from negative-ion ESI FT-ICR MS. Contour plots consolidate large amounts of data and display alkylation (carbon number) and aromaticity (DBE) properties and trends.
Field Desorption Ionization for Analysis of Non-Polar and Low-Polarity Compounds

While electrospray selectively ionizes the most polar species in petroleum, it cannot ionize the non-polar hydrocarbon molecules that make up the bulk of petroleum liquids. Hydrocarbons in petroleum include paraffins (saturated alkanes), cycloparaffins, aromatic hydrocarbons and polyaromatic hydrocarbons. The later three contain many paraffinic side chains that extend from the core molecule. In addition, non-polar and/or low-polarity sulfur species, which include thiols, sulfides and thiophenes, are not accessible by conventional ESI.

Field desorption/field ionization (FD/FI) efficiently ionize nonpolar molecules, and FD/FI mass spectrometry have been used extensively in the past to characterize hydrocarbons in petroleum mixtures.\(^7\), \(^22\)-\(^25\). The ultrahigh resolution and mass accuracy of FT-ICR MS were first applied to hydrocarbon characterization with electron impact ionization.\(^13\), \(^14\) Subsequently, a high field FD/FI FT-ICR MS system has been constructed at the National High Magnetic Field Laboratory (NHMFL) and used to characterize an assortment of petroleum samples.\(^26\)-\(^29\)

FD/FI are “soft” ionization techniques that ionizes a wide range of petroleum molecules. FD/FI ionization occurs when analyte molecules are subjected to a strong electric field (~10\(^8\) V/cm) at the tips of carbon micro-needle dendrites on the FD/FI emitter (Figure 1.5).\(^30\)
The electric field is established by application of -10 kV (for positive ions) to the counter electrode shown in Fig. 1.8. In FI, gaseous analyte ions flow past the the high electric field at the emitter tips, whereas for FD the analyte is applied directly to the emitter and desorbed by the electric field with thermal assistance. FD/FI generate true molecular ions, M⁺⁺, by electron tunneling, rather than quasimolecular ions formed in ESI. FD requires no samples matrix, which yields very clean mass spectra. In addition, FD can desorb and ionize the nondistillable petroleum “bottoms” that remain after refining. The advent of the liquid injection field desorption ionization (LIFDI) probe allows multiple sample applications without the need to break vacuum.
All FD FT-ICR experiments in Chapters 2, 4, and 8 were performed on a 9.4 Tesla FD FT-ICR mass spectrometer shown in Figure 1.6 and described in detail elsewhere. Briefly, ions were generated externally by a commercial LIFDI probe (Linden CMS, Leeste, Germany). Sample was applied by immersion of the atmospheric side of the fused silica capillary into the sample solution (typically 1 mg/mL in methylene chloride), and the pressure differential forced the liquid into the vacuum chamber where it was deposited on the emitter. Ions were accumulated in a linear octopole ion trap for 1-20 seconds before transfer across three stages of differential pumping to an open cylindrical capacitively coupled Penning ion trap. If needed, trapped ions were cooled with helium collision gas, delivered by a solenoid pulse valve, before excitation. Broadband frequency sweep (chirp) excitation was followed by direct mode image current detection that yielded a 4 Mword time-domain data. Single scan or co-added (2-100) time-domain data sets were Hanning apodized and zero-filled once before fast Fourier transform and magnitude calculation. Frequency was converted to mass-to-charge ratio as previously described and data was exported to a spreadsheet for reduction. A modular ICR data system (MIDAS) data station handled instrument control, data acquisition and data analysis.
Recent advances in atmospheric pressure photoionization (APPI) and chemical derivatization have allowed additional characterization of non-polar and low-polarity species in crude oil. APPI is well suited for the characterization of non-polar sulfur and hydrocarbons; specifically aromatic ring systems. APPI also efficiently ionizes nitrogen species and yields highly complex mass spectra for petroleum samples. Like ESI, APPI is a continuous ionization source, and is easily coupled to most commercial and custom-built mass spectrometers. Chemical derivatization of non-polar sulfur to the methyl sulfonium salt allows analysis by ESI FT-ICR MS. However, there appear to be limitations to chemical derivatization for the characterization of heavy feedstocks and petroleum residues.
Electrospray Ionization for Analysis of Polar Compounds

Petroleum liquids are composed primarily of pure hydrocarbons (~85-95 %, by weight), while polar and slightly polar N, S, and O containing species only represent ~ 5-15 %. However, these polar species are the cause of many costly production and processing problems. Fenn and Zhan discovered that the most polar constituents of are easily ionized by electrospray ionization (ESI) and detected by mass spectrometry. This discovery quickly launched the extensive characterization of polar components of petroleum by ESI FT-ICR MS in the Marshall group at the NHMFL.

ESI is a “soft” ionization technique that produces little to no analyte fragmentation. The electrospray process also produces quasimolecular ((M-H)\(^{-}\) and (M+H)\(^{+}\)) ions at atmospheric pressure, which enables multiple samples to be run without the need to break vacuum. Figure 1.7 shows a typical ESI source schematic. Briefly, a high negative (or positive) potential (Typically 0.5-4 kV) is applied across an electrospray needle and a counter electrode. The electric field causes the ions of interest to migrate to and out of the electrospray needle, where a Taylor cone is formed. As charge builds up, the Taylor cone releases charged droplets. Evaporation of the droplets forces the charged analytes closer together until the Rayleigh limit is reached and the droplet breaks apart in what is termed a “Coulombic explosion”. This process continues until no solvent remains, after which the charged analytes are accelerated towards the opposite charge of the counter electrode and thus into the mass spectrometer. The “Coulombic explosion” mechanism is easily explained, however it should be noted that the mechanism by which gas-phased ions are produced from the charged droplets is still under debate.
Figure 1.7: Schematic for negative ion electrospray ionization. For positive ion electrospray ionization, the polarity of the high voltage power supply is reversed.

Figure 1.8 shows representative structures and lists typical petroleum compounds ionized and detected by ESI FT-ICR MS. It should be noted that the compounds in Fig. 1.6 usually contain paraffinic chains that extend from the core structure. Negative-ion mode ESI selectively ionizes acidic compounds in petroleum such as carboxylic acids, phenols and neutral (pyrrole derivatives) nitrogen compounds. Carboxylic acids are present as saturated, acyclic, naphthenic, aromatic and polyaromatic acids.\textsuperscript{48} Carboxylic acids in crude oil (also collectively called naphthenic acids) contribute to liquid-phase corrosion in processing and refining.\textsuperscript{49} Nitrogen compounds have been found to effect fuel instability during storage.\textsuperscript{50, 51}
Positive-ion mode ESI selectively ionizes basic nitrogen (pyridine derivatives), some primary amines and sulfoxides in petroleum. Basic nitrogen compounds are known to deactivate hydrotreatment catalysts used for sulfur removal.\textsuperscript{52} Both modes also ionize multi-heteroatom containing species such as \(N_xS_x\), \(N_xO_x\), and \(S_xO_x\), as long as there is one ionizable heteroatom. Heteroatom containing molecules increase in abundance with an increase in the boiling point fraction. Additionally, species that are not ionized by normal electrospray (i.e. non-polar sulfur such as sulfides and thiophenes) can be chemically derivatized to methylated species accessible by electrospray.\textsuperscript{40, 41}

Figure 1.8: Polar species selectively ionized and detected by ESI FT-ICR MS. Structures are representative; all species contain paraffinic chains that extend from the core molecule.
All electrospray experiment in Chapters 3-8 were performed on a custom-built 9.4 Tesla ESI FT-ICR mass spectrometer (Figure 1.9) that has been described in detail elsewhere.\textsuperscript{53, 54} Petroleum samples are typically diluted to 1 mg/mL in 50:50 (v/v) toluene:methanol solution. To ensure efficient ionization, 1\% (by volume, \textasciitilde 65 fM) of ammonium hydroxide/acetic acid was added for positive/negative ion mode. A syringe pump delivered sample solution to a fused silica micro-electrospray needle.\textsuperscript{55} Ions were accumulated externally in a linear octopole ion trap for 1-60 seconds before transfer across four stages of differential pumping by rf-only multipoles to an open cylindrical Penning ion trap.\textsuperscript{33} Broadband frequency-sweep (chirp) dipolar excitation\textsuperscript{12, 35} was followed by direct mode image current detection that yielded a 4 Mword time-domain data. Typically, 50-200 time-domain data sets were co-added, followed by a Hanning apodization and a single zero-fill before fast Fourier transform and magnitude calculation. Frequency was converted to mass-to-charge ratio as described above and the data was exported to a spreadsheet for reduction. A modular ICR data system (MIDAS) data station handled instrument control, data acquisition and data analysis.\textsuperscript{36, 37}
Figure 1.9: Schematic of the 9.4 Tesla passively shielded electrospray ionization FT-ICR mass spectrometer at the NHMFL. All ESI experiments described in Chapters 3-8 were performed on this system. Pressures in the various pumping stages (from left to right, source to cell) are $10^{-3}$, $10^{-6}$, $10^{-8}$ and $10^{-10}$ Torr.
CHAPTER 2.

AUTOMATED LIQUID INJECTION FIELD DESORPTION IONIZATION FOR FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

Summary

We describe the automation of liquid injection field desorption ionization (LIFDI) for reproducible sample application, improved spectral quality and high throughput analyses. A commercial auto-sampler provides reproducible and unattended sample application. A custom built field desorption (FD) controller allows data station or front panel control of source parameters including high voltage limit/ramp rate, emitter heating current limit/ramp rate and feedback control of emitter heating current based on ion current measurement. Automated LIFDI allows ensemble averaging of hundreds of Fourier transform ion cyclotron resonance (FT-ICR) mass spectra for increased dynamic range, mass accuracy and S/N ratio (for a given time domain length and mass resolving power) over single application FD experiments, as shown here for a South American crude oil. This configuration can be adapted to any mass spectrometer with a LIFDI probe.

Introduction

Field desorption (FD) ionizes a variety of non-volatile analytes. FD is a “soft” ionization technique, yielding predominantly intact M+• molecular ions for a wide range of compound classes, such as saturated/aromatic hydrocarbons and non-polar (e.g. thiophenic) sulfur not accessible by electrospray ionization. The pulsed nature of the FD ionization source, combined with the need to reapply sample after every experiment, makes high throughput analyses difficult. The advent of LIFDI enabled in vacuo sample application; i.e. sample is applied without the need to break vacuum. LIFDI has been used for many sample types
including petroleum mixtures\textsuperscript{26, 28, 66-68}, metal complexes\textsuperscript{65, 69-71}, and fullerenes\textsuperscript{72, 73}.

The complexity of hydrocarbon mixtures requires ultra-high mass resolving power (m/\Delta m\textsubscript{50\%} > 300,000) and sub-ppm (< 500 ppb) mass accuracy. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) allows assignment of a unique elemental composition to each ion signal observed in complex mass spectra of petroleum samples. Optimum mass resolving power and mass accuracy are realized for small trapped ion populations in the ICR cell and low trap plate voltage (e.g. <1 V). Continuous ion production by electrospray\textsuperscript{18, 43, 74, 75} or atmospheric pressure photoionization\textsuperscript{38, 39, 41} allows ensemble averaging of 100-500 measurements at optimal resolving power (achieved for low ion number and trap plate voltage) and increases signal-to-noise ratio (S/N). However, the pulsed nature of a traditional FD experiment, which arises from the need to periodically reapply sample, makes ensemble averaging difficult.

Early FD FT-ICR MS experiments required manual sample application, manual control of FD ionization parameters and produced a single mass spectrum for each sample application. In order to maximize resolving power and S/N ratio for single measurements, those experiments employed a helium gas pulse to cool ions trapped in the ICR cell prior to FT-ICR excitation/detection, which added ~30 seconds to each measurement cycle (for evacuation of the helium collision gas).\textsuperscript{29} Continuous-flow sample introduction partially overcomes the problem of transient FD ion production and can supply continuous ion current for extended periods (up to one hour).\textsuperscript{27} However, continuous-flow sample introduction proved to be problematic for heavy end petroleum samples and source conditions must be optimized for each sample. Alternatively, automation of traditional LIFDI allows for the co-addition of several hundred mass spectra, allows the FD emitter to be cleaned between
measurements, and enables unattended analysis of one or multiple samples.\textsuperscript{76, 77}

Here, we introduce fully automated LIFDI FT-ICR MS to allow ensemble averaging of over two hundred mass spectra of a South American crude oil. Automated LIFDI allows multiple FT-ICR measurements at low ion number and trap plate voltage to improve spectral quality. Mass accuracy, S/N ratio and dynamic range all improve versus optimized single measurement experiments. FD automation is reproducible, allows unattended operation and only minimal optimization is needed for various sample types. Although this paper focuses on FT-ICR MS, the automated LIFDI configuration is suitable for coupling to any mass spectrometer equipped with a LIFDI probe.

**Experimental Methods**

The experimental setup for automated LIFDI is show in Figure 2.1. A modular ICR data acquisition and analysis system (MIDAS) data station\textsuperscript{36, 37} controls the mass spectrometer and a custom built FD controller. The auto-sampler is controlled by a stand-alone PC and receives a TTL trigger from the data station.

The system uses a commercial liquid injection field desorption (LIFDI) probe (Linden CMS, Leeste, Germany).\textsuperscript{32} Figure 2.2 shows the interface of the HTS PAL auto-sampler to the LIFDI probe. A 1.5 m, 75 \(\mu\)m i.d. fused silica capillary (Polymicro Technologies, LLC, Phoenix, AZ) runs the length of the LIFDI probe from the HTS PAL auto-sampler (LEAP Technologies, Carrboro, NC) to the FD emitter and allows in vacuo sample application. A custom syringe holder attaches the fused silica capillary to the HTS PAL XYZ robot (see inset in Figure 2.2).
Figure 2.1: Schematic of automated LIFDI experimental setup. The MIDAS Predator data station supplies a TTL trigger to initiate the auto-sampler, controls the field desorption controller and handles instrument control and data acquisition.

A custom built field desorption controller allows for front panel or data station control of field desorption ionization parameters. Three 0-10 V inputs to the field desorption controller set high voltage limit/ramp rate, emitter heating current (EHC) limit/ramp rate and feedback control of EHC based on total ion current (as measured at the FD counter electrode). The data station triggers onset of high voltage and emitter heating current. Total ion current, heating current and high voltage can be digitally monitored at the data station or by panel meters on the field desorption controller.
A South American crude oil was used to optimize automation parameters. All experiments were performed with a custom-built FD FT-ICR mass spectrometer, operated in a 9.4 T, 155 mm horizontal bore diameter actively shielded superconducting solenoidal magnet (Magnex Scientific, Oxford, England). A TTL pulse (supplied by the MIDAS data station) initiates sample application where the fused silica capillary is dipped into dilute sample solution (0.01-0.1 mg/mL) for 1-5 seconds. The pressure differential created by the source chamber vacuum moves the plug of sample solution through the fused silica capillary. After the sample solution transverses the capillary and is deposited on the field desorption emitter, the atmospheric end of the capillary is butted onto septum material to reduce airflow through the capillary.
elastic septum material to reduce airflow through the capillary. A 15 second delay allows evacuation of solvent before a 15 kV/s voltage ramp to 10 kV followed by an optional emitter heating current ramp (0-150 mA/s) to a maximum of 150 mA. After ionization, positive ions are transported through a short 76 mm octopole ion guide to a 160 mm storage octopole where ions are accumulated for 5-30 s and helium gas is introduced to facilitate collisional cooling of the ions. Ions are extracted from the accumulation octopole with the aid of wire extraction electrodes\(^{78}\) and are transported via a 145 cm octopole to a capacitively coupled\(^ {34}\) open cylindrical Penning ion trap.\(^ {33}\) Ions are excited via broadband frequency sweep (chirp) dipolar excitation and detected by direct mode image current detection to produce 4 Mword time-domain data sets. The emitter heating current is ramped to 100 mA (~ after each measurement to clean off excess sample before the next sample deposition.

LIFDI FT-ICR MS mass spectra were internally calibrated with respect to a high abundance hydrocarbon homologous series present in each sample.\(^ {26}\) Singly charged ions (200 < \(m/z\) < 1000) with a relative abundance greater than eight times the standard deviation of baseline noise (8\(\sigma\)) were exported to a spreadsheet. Measured masses were converted from the IUPAC mass scale to the Kendrick mass scale\(^ {19}\) for identification of homologous series and peak assignment by Kendrick mass defect analysis.\(^ {20}\)

**Results and Discussion**

In order to avoid sample build up on the FD emitter, the sample concentration must be reduced from the 1 mg/mL used for single measurement experiments. For petroleum-derived samples the acceptable sample concentration for automated LIFDI is 0.01-0.5 mg/mL and is sample dependent (i.e. “heavier” samples require more dilution). The South American crude oil was diluted to 0.05 mg/mL. **Figure 2.3**
shows broadband LIFDI FT-ICR mass spectra for 100 co-added experiments (Fig. 2.3 top; 0.05 mg/mL, 0-40 mA EHC (~0-325 °C)) and an optimized single experiment (Fig. 2.3 bottom; 1 mg/mL, 20 mA EHC (~75 °C), with helium cooling gas pulse) of South American crude oil.

Figure 2.3: Broadband automated LIFDI FT-ICR MS (top; 100 averaged experiments, 0.05 mg/mL, 0-40 mA EHC) and an optimized single experiment (bottom; 1 mg/mL, 20 mA EHC) LIFDI FT-ICR mass spectra of a South American crude oil. The automated LIFDI FT-ICR MS shows an extended mass range over the single experiment. Insets show increase in S/N at high m/z.

Single experiment mass spectra that employ wide emitter temperature gradients (e.g. 0-40 mA EHC) result in large ion populations in the mutlipole storage/ion guides and subsequent m/z discrimination due to space charge effects. Similarly, the decrease in the number of produced ions for automated LIFDI experiments minimizes m/z discrimination in the multipole ion-guides and results in a wider m/z range transferred to the ICR cell. In addition, higher EHC allows a wider range of desorption
temperatures to facilitate ionization of higher boiling components. Finally, S/N lost to low ion population is recovered by ensemble averaging and results in detection of low abundance ion signals at low and high m/z. Insets in Figure 2.3 show increase in S/N ratio for high m/z species with automated LIFDI (a similar effect is observed at low m/z). Table 2.1 shows the improvements realized by signal averaging versus a single experiment. The mass accuracy for all assigned elemental compositions is improved through replicate measurement and increased S/N for low abundance species. Dynamic range improvement is dramatic for automated LIFDI; realized here by a 40% increase in the number of observed peaks.

Table 2.1: Figures of Merit for 100 Averaged Experiments and a Single Experiment

<table>
<thead>
<tr>
<th></th>
<th>100 Averaged Experiments</th>
<th>Single Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Mass Resolving Power</td>
<td>437 040</td>
<td>410 495</td>
</tr>
<tr>
<td>Assignment RMS Error (ppb)</td>
<td>104</td>
<td>166</td>
</tr>
<tr>
<td>Peak Number (5σ)</td>
<td>5,954</td>
<td>4,109</td>
</tr>
</tbody>
</table>

Co-addition of multiple measurements increases the level of detail and dynamic range for LIFDI of petroleum samples. Figure 2.4 shows the class distribution (heteroatom content) for South American crude oil derived from the spectra shown in Figure 2.3. The hydrocarbon class has the highest relative abundance for both experiments, followed by the S₁ class. Class distribution is similar for both experiments, however low abundance classes (O₂ and S₁O₁) that are not seen in a single experiment are observable with ensemble averaging.
Figure 2.4: Heteroatom class distribution (heteroatom content) for South American crude oil derived from the LIFDI FT-ICR mass spectra in Figure 2.3. Signal averaging yields the low abundance classes $O_4$ and $S_1O_1$.

Isoabundace color-coded plots of double bond equivalents (DBE (number of rings and/or double bonds)) versus the carbon number are shown in **Figure 2.5** for the hydrocarbon class (Fig. 2.5 top) and the $S_1$ class (Fig. 2.5 bottom). Plots derived from the co-added spectrum (Fig. 2.5 left) show wider carbon number distributions versus those from a single measurement (Fig. 2.5 right) due to the increase in S/N for low abundance species at low and high mass. The hydrocarbon class extends from carbon number 17-55 for the co-added spectrum (Fig. 2.5, top left), whereas a single experiment yields a carbon number distribution of 18-48 (Fig. 2.5, top right). Similarly, the $S_1$ carbon number distribution for the co-added spectrum ranges from 21-52 (Fig. 2.5, bottom left) and the single experiment carbon number ranges from 21-44 (Fig. 2.5, bottom right). More aromatic species (higher DBE) are
also enhanced in the co-added spectrum due to the ability to collect ions over an extended heating range. Hydrocarbons in the co-added spectrum range from DBE 1-16 (Fig. 2.5, top left) and the single experiment spectrum ranges from DBE 1-14 (Fig. 2.5, top right). The S<sub>1</sub> class for the co-added spectrum extends from DBE 2-17 (Fig. 2.5, bottom left), whereas the single experiment spectrum ranges from DBE 2-16 (Fig. 2.5, bottom right).

Figure 2.5: Color-coded isoabundance contours for plots of double-bond equivalents (DBE) versus the carbon number for the hydrocarbon class (top) and S<sub>1</sub> class (bottom) derived from the LIFDI FT-ICR mass spectra in Figure 2.3. Automated LIFDI FT-ICR MS (left) allows more detailed characterization than single experiment LIFDI FT-ICR MS (right).
Conclusions

Automated LIFDI FT-ICR MS allows the ensemble averaging of multiple mass spectra for improved dynamic range, mass resolving power and mass accuracy over single application experiments. Thus, more detailed compositional analysis of non-polar and low-polarity species in complex mixtures is now possible. Samples can be analyzed unattended and the auto-sampler allows the analysis of multiple samples per experiment. The new FD controller and the use of an auto-sampler allow fine control of FD ionization parameters for improved reproducibility. The automation setup is robust and allows analysis of any sample that can be analyzed by traditional single application FD. Any system equipped with a LIFDI probe can easily be modified for the described automation setup.
CHAPTER 3.
CHARACTERIZATION OF ACIDIC SPECIES IN ATHABASCA BITUMEN AND BITUMEN HEAVY VACUUM GAS OIL BY NEGATIVE-ION ESI FT-ICR MS WITH AND WITHOUT ACID-IER PREFRACTIONATION

Summary

Because acids in petroleum materials are known to corrode processing equipment, highly acidic oils are sold at a discount (based on their total acid number (TAN)). Here, we identify the acidic species in raw Canadian bitumen (Athabasca oil sands) and its distilled heavy vacuum gas oil (HVGO) as well as acid-only and acid free fractions isolated by use of an ion-exchange resin (Acid-IER) by negative-ion ESI FT-ICR mass spectrometry.

The ultrahigh mass resolving power \((m/\Delta m_{50\%} > 350,000)\) and high mass accuracy (better than 500 ppb) of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), along with Kendrick mass sorting, enable the assignment of a unique elemental composition to each peak in the mass spectrum. Acidic species are characterized by class (NnOoSs heteroatom content), type (number of rings plus double bonds, or double bond equivalents, DBE), and carbon number distribution. We conclude that the analytical capability of FT-ICR MS and the selectivity of the electrospray ionization process eliminate the need for acid fractionation to characterize naphthenic acids in bitume. However, because the acid-free fraction (not retained on the Acid-IER) contains SXOX heteroatomic classes not observed in the parent bitumen, acid-IER fractionation does help to identify such low-abundance species. Further, we observe that a majority of the acids identified in the parent bitumen distill into the HVGO fraction. Variations in the carbon number and aromaticity of the classes are discussed in detail.
Introduction

Oil sands bitumen deposits in Alberta, Canada represent a substantial reserve of recoverable crude oil: an estimated 175 billion barrels, second only to Saudi Arabia with ~ 260 billion barrels of recoverable crude oil. These deposits are either extracted from sand after conventional mining, or brought to the surface by in situ techniques such as steam assisted gravity drainage (SAGD). Mined and SAGD bitumen are highly viscous (>100,000 cP) and have low API gravity values (7-15\textdegree), and cannot be transported by pipeline. Diluents such as natural gas condensate or synthetic diluents are added to bitumen to reduce viscosity (350 cSt) and density (0.94 g/cm3) for pipeline transportation.

Solid contaminants and minor organic components of bitumen and heavy oils play a major role in the refinery processing of these feedstocks. Organic acids known as "naphthenic acids" constitute a small portion of the total bitumen. However, those components are known to be corrosive in refinery operations. A crude oil is typically deemed safe for refining according to its total acid number (TAN). TAN is defined as the quantity of base (in mg of KOH) required to neutralize all acidic species in one gram of sample. Many refineries refuse to process crude oils with TAN greater than 0.5 mg KOH/g oil and streams with TAN greater than 1.5 mg KOH/g oil, because of their refinery metallurgy. Athabasca bitumen has a TAN of ~3.2-5.5 mg KOH/g oil (i.e., well above the accepted limit). Accurate TAN determination by ASTM 664 is difficult due to the high viscosity of Athabasca bitumen. It is not clear how much (if any) of this increased TAN contributes to refinery corrosion. Reports and data on refinery corrosion due to naphthenic acids in oil sands processing is limited and is a matter of controversy. In any case, Athabasca crude is penalized in market price because of its high TAN number. Naphthenic acids may not be the sole cause of high TAN
and/or high corrosivity, because some sulfur compounds have been shown to affect corrosivity and TAN values.\textsuperscript{81, 82}

Techniques used to characterize petroleum acids include Fourier transform infrared spectroscopy,\textsuperscript{83-85} 13C nuclear magnetic resonance,\textsuperscript{84, 85} two-dimensional gas chromatography,\textsuperscript{86} hyphenated mass spectrometric techniques such as GC-MS\textsuperscript{87-89} and LC-MS\textsuperscript{90}, and liquid-secondary ion mass spectrometry\textsuperscript{91}. Ionization techniques for mass spectrometry have included fast atom bombardment (FAB),\textsuperscript{92-94} chemical ionization,\textsuperscript{91} atmospheric pressure chemical ionization (APCI),\textsuperscript{84, 91} electrospray ionization (ESI),\textsuperscript{74, 84, 91} field desorption ionization,\textsuperscript{29} and atmospheric pressure photoionization.\textsuperscript{38}

The advantages of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS\textsuperscript{3}) for the analysis of complex petroleum mixtures are well documented.\textsuperscript{18, 29, 38, 41, 74, 75, 95, 96} Briefly, such measurements make possible the correlation (and ultimately prediction) of the properties and behavior of petroleum and its products--a field now known as "petroleomics."\textsuperscript{4, 5, 97} Here, we exploit the selectivity of negative-ion electrospray ionization to provide heteroatom class (NnOoSs), type (double bond equivalents (DBE = number of rings plus double bonds involving carbon)) and carbon number analysis for the organic acids in raw Athabasca bitumen, its distilled heavy vacuum gas oil (HVGO) fraction, and acid-only and acid-free fractions of the HVGO isolated by use of an ion-exchange resin (IER). We discuss the advantages of IER isolation of naphthenic acids as well as common features of the various acid distributions.
Experimental Methods

Sample Description and Bulk Property Measurements

Athabasca bitumen was obtained from the oil sands mining operation in Fort McMurray, Alberta, Canada. The heavy gas oil fraction (HVGO) of approximately 30 wt% (boiling range, 350-525°C) was obtained by ASTM D1160 distillation. TAN was measured by the ASTM D-664 method and molecular weights were determined by vapor pressure osmometry at 120 °C in o-dichlorobenzene. Naphthenic acids were separated from the heavy vacuum gas oil fraction by the acid-IER method. Calculated TAN for the acid-only and acid-free fractions was determined by: ((fraction % recovery * measured TAN)/100).

Sample Preparation for ESI FT-ICR MS

Samples solutions were prepared to ~1 mg/mL in 50:50 toluene:methanol. Ten microliters of ammonium hydroxide was added to each 1 mL of sample solution to ensure efficient deprotonation for negative-ion electrospray analysis. All solvents were HPLC grade (Fisher Scientific, Pittsburgh, PA).

Instrumentation

All electrospray FT-ICR MS experiments were performed on the 9.4 T ESI FT-ICR mass spectrometer described in Chapter 1. FT-ICR m/z range coverage was verified by comparison to low-resolution mass spectra were acquired with a linear quadrupole ion trap mass spectrometer (LTQ, Thermo Electron Corp., San Jose, CA) under negative-ion electrospray conditions analogous to those described in Chapter 1.
Mass Calibration and Data Analysis

FT-ICR mass spectra were internally calibrated with respect to a high abundance homologous series of ions each containing two oxygen atoms present in each sample, as previously described. The m/z values (for singly charged ions) of 300-900 Da with a relative abundance greater than six times the standard deviation of the baseline noise were exported to a spreadsheet. Measured masses were converted from the IUPAC mass scale to Kendrick mass scale and sorted according to Kendrick mass defect values to facilitate identification of homologous series. Peak assignments were performed by Kendrick mass defect analysis as previously reported.

Results and Discussion

Feedstock Properties

Table 3.1 summarizes the bulk properties of the samples analyzed by FT-ICR MS. The bitumen and its HVGO fraction exhibit relatively high sulfur and low oxygen content, whereas the oxygen content of the acid-only fraction is very high. The IER-separated acid from the HVGO accounts for approximately 3 wt% and is assumed to contain entirely naphthenic acids. Since HVGO is about 30 wt% of bitumen the naphthenic acid content is about 1 wt% of total bitumen. The good agreement between the measured HVGO TAN and calculated TAN for the acid-only fraction suggests that most acidic species in the HVGO are naphthenic in nature. Although the molecular weights of all the components shown in Table 3.1 were measured in a polar solvent and at high temperature to prevent aggregation (hydrogen bonding), the acid fraction showed higher molecular weight than the HVGO due to the
removal of lower molecular weight hydrocarbons in the non-acidic fraction by the IER extraction.

Table 3.1: Feedstocks Bulk Properties

<table>
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<tr>
<th>Feedstock</th>
<th>H/C</th>
<th>N(wt%)</th>
<th>S(wt%)</th>
<th>O(wt%)</th>
<th>Wt%</th>
<th>Measured TAN (mg KOH/g oil)</th>
<th>Calculated TAN (mg KOH/g oil)</th>
<th>MW (g/mol)</th>
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<tr>
<td>Athabasca Bitumen</td>
<td>1.41</td>
<td>0.41</td>
<td>4.90</td>
<td>1.28</td>
<td>5.58</td>
<td></td>
<td></td>
<td>557</td>
</tr>
<tr>
<td>HVGO</td>
<td>1.47</td>
<td>0.14</td>
<td>3.48</td>
<td>0.83</td>
<td>4.32</td>
<td></td>
<td></td>
<td>345</td>
</tr>
<tr>
<td>HVGO Acid-Only</td>
<td>1.75</td>
<td>0.12</td>
<td>1.28</td>
<td>9.12</td>
<td>2.96</td>
<td>135.7</td>
<td>4.02</td>
<td>541</td>
</tr>
<tr>
<td>HVGO Acid-Free</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>97.04</td>
<td>0.31</td>
<td>0.3</td>
<td>357</td>
</tr>
</tbody>
</table>

Mass Spectrometric Analysis

Naphthenic Acids in Bitumen vs. HVGO and Ion-Exchange Fractions

Figure 3.1 shows broadband negative-ion electrospray FT-ICR mass spectra of the four samples. More than 4,000 raw bitumen species were resolved and identified, compared to >1,000 for the HVGO and HVGO acid-only fraction and >2,000 for the HVGO acid-free fraction. All observed ions are singly charged, as evidenced by the observed unit m/z difference between $^{12}\text{C}_c$ and $^{13}\text{C}_{12}\text{C}_{c-1}$ signals for each elemental composition. The average mass resolving power (m/$\Delta m_{50\%}$) was greater than 400,000 in all cases: namely, sufficient to resolve the 3.4 mDa mass doublet for species whose elemental compositions differ by SH$_4$ vs. C$_3$ across the entire observed mass range. The molecular weight range is largest for the raw bitumen. The HVGO, HVGO acid-only fraction and HVGO acid-free fraction do not contain the
Figure 3.1: Broadband negative-ion electrospray 9.4 T FT-ICR mass spectra of Athabasca Canadian bitumen, distillation isolated heavy vacuum gas oil (HVGO), IER-isolated HVGO acid-fraction, and IER-isolated HVGO acid-free fraction. Insets at right show low resolution linear ion trap mass spectra that verify the molecular weight distributions observed by FT-ICR MS.
higher molecular weight species (700 < m/z < 900) present in the raw bitumen. The HVGO and IER-fraction exhibit narrower molecular weight distributions because their compositions are limited by distillation cut temperature. The insets in Figure 3.1 show low-resolution linear quadrupole ion-trap mass spectra that provide independent verification of the molecular weight distributions obtained by FT-ICR MS.

Molecular formulas could be assigned to 95% of all observed species. From the molecular formula assignments, complete class \((N_nO_oS_s\) heteroatom content), type (the number of rings and double bonds; double bond equivalents (DBE)) and carbon number analyses are straightforward. **Figure 3.2** shows the class distribution for raw bitumen, HVGO, and the IER-isolated acid-only and acid-free fractions. The \(O_2\) class contains naphthenic acids, which predominate in all but the HVGO acid-free fraction. The similarity in class distribution between the raw bitumen, HVGO, and HVGO acid-fraction suggests that naphthenic acid composition may be determined from the FT-ICR MS analysis of the raw bitumen alone, so that further fractionation and/or purification is unnecessary.

Furthermore, most \(O_2\) and \(S_1O_2\) acids distill from the bitumen to the HVGO fraction. Acid-IER fractionation enables identification of \(S_1O_4\) and \(S_2O_4\) multi-heteroatom classes (in the HVGO acid-free fraction) that were not observed in the HVGO; due to removal of high relative abundance \(O_2\) species. In addition, the HVGO acid-free fraction also contained low abundance \(S_1O_5\) through \(S_1O_8\) series (data not shown). The presence of these \(S_XO_X\) species in the acid-free fraction suggests non-carboxylic (or sulfonic) acid functionalities, because sulfur-based acids would not be retained on the Acid-IER resin. We are currently trying to identify the \(S_XO_X\) functionalities. Low abundance, non-carboxylic acid-containing classes such as \(N_1O_1\), \(N_1S_1\), and \(S_1O_1\) distill into the HVGO and are subsequently identified in the HVGO acid-free fraction. To provide a more detailed look at acid composition, the data in
Fig. 3.2 was used to construct isoabundance color-coded plots to investigate the differences in DBE and carbon number composition of the samples.

**Bitumen Class Analysis: Negative-Ion ESI FT-ICR MS**

![Graph](image)

**Class**

- Athabasca Bitumen
- HVGO
- HVGO Acid-Only Fraction
- HVGO Acid-Free Fraction

**Relative Abundance (% total)**

- 0
- 10
- 20
- 30
- 40
- 50
- 60
- 70
- 80
- 90
- 100

**Figure 3.2:** Heteroatom class distribution (heteroatom content) for Athabasca Canadian bitumen, HVGO, IER-isolated HVGO acid-fraction, and IER-isolated HVGO acid-free fraction, derived from the high-resolution ESI FT-ICR mass spectra of Fig. 3.1.

**DBE vs. Carbon Number for O2 Class Species**

**Figure 3.3** shows color-coded isoabundance contours for double bond equivalents versus carbon number for members of the O2 class. Raw bitumen mainly contains acids from DBE 1-10 with ~25-46 carbons. The highest relative abundance acids are non-aromatic (DBE 2-4 (consistent with a structure of two cyclic alkane rings and a carboxylic acid), with 25-40 carbons, centered at ~32 carbons. Acids from HVGO display narrower DBE (2-7) and carbon number ranges (26-
40) than raw bitumen, suggesting that the higher molecular weight and/or more aromatic acids do not distill into the HVGO fraction.

**O₂ Class: Negative-Ion ESI FT-ICR MS**

![Graphs showing distribution of DBE vs. carbon number for different fractions](image)

Figure 3.3: Color-coded isoabundance contours for plots of double bond equivalents (DBE) vs. carbon number for the O₂ class for Athabasca Canadian bitumen (top left), HVGO (top right), IER-isolated HVGO acid-fraction (bottom left) and IER-isolated HVGO acid-free fraction (bottom right).

The HVGO acid-only fraction O₂ species extend to slightly higher carbon number than those from HVGO, and lower carbon number than for raw bitumen and HVGO, suggesting that shorter alkyl-chain, less sterically hindered naphthenic acids may preferentially bind to the the Acid-IER. A few "acids" are not retained by IER and elute in the acid-free fraction. In contract, the HVGO acid-free fraction exhibits more extensively aromatic O₂ species (DBE 7-11) that are not visible from raw bitumen. The high DBE species could arise from low-acidity phenols (a phenyl ring with an ionizable hydroxyl group) or a phenol combined with
a furan (oxygen contained in a five member ring) that are thought to exist in the parent bitumen.

**DBE vs. Carbon Number for S$_{1}$O$_{2}$ Class Species.**

**Figure 3.4** shows isoabundance contours for DBE versus carbon number for the S$_{1}$O$_{2}$ class.

Figure 3.4: Color-coded isoabundance contours for plots of double bond equivalents (DBE) vs. carbon number for the S$_{1}$O$_{2}$ class for Athabasca Canadian bitumen (top left), HVGO (top right), IER-isolated HVGO acid-fraction (bottom left) and IER-isolated HVGO acid-free fraction (bottom right).

Raw bitumen contains S$_{1}$O$_{2}$ species with DBE 4-11 and carbon number 27-46. The two regions of higher relative abundance (DBE 4-7 and carbon numbers of 28-34; DBE 7-11 and carbon numbers of 37-42) indicate two stable core structures, consistent with thiophenic and benzothiophenic acids. Unlike the O$_{2}$ class, only a subset of the S$_{1}$O$_{2}$
class identified in the raw bitumen distills into the HVGO fraction, corresponding to \( \text{S}_1 \text{O}_2 \) species of DBE 3-8 and carbon numbers 25-35. The species of high relative abundance are similar to those for bitumen but with less aromatic cores. As for the \( \text{O}_2 \) class, the HVGO acid-only fraction \( \text{S}_1 \text{O}_2 \) species have DBE values similar to those for HVGO but with somewhat larger carbon numbers. The \( \text{S}_1 \text{O}_2 \) species are presumed to contain acid functionalities, because they are less abundant in the acid-free fraction.

**DBE vs. Carbon Number for \( \text{N}_1 \) Class Species**

**Figure 3.5** shows plots of \( \text{N}_1 \) class DBE versus carbon number.

![Color-coded isoabundance contours for plots of double bond equivalents (DBE) vs. carbon number for the \( \text{N}_1 \) class for Athabasca Canadian bitumen (top left), HVGO (top right), IER-isolated HVGO acid-fraction (bottom left) and IER-isolated HVGO acid-free fraction (bottom right).](image-url)

**Figure 3.5**: Color-coded isoabundance contours for plots of double bond equivalents (DBE) vs. carbon number for the \( \text{N}_1 \) class for Athabasca Canadian bitumen (top left), HVGO (top right), IER-isolated HVGO acid-fraction (bottom left) and IER-isolated HVGO acid-free fraction (bottom right).
The N$_1$ species (pyrrolic ("neutral") nitrogen) in raw bitumen are highly aromatic, with DBE values from 10-18 and carbon numbers of 32-46. The most abundant species exhibit DBE 13 (consistent with a core structure of 5H-Benzob[1]carbazole with an additional cyclic alkane ring). The DBE and carbon number distributions for the HVGO are narrower than for raw bitumen: the most abundant N$_1$ species (DBE 12-13) do not contain the high carbon number species found in the raw bitumen. Few nitrogen species are extracted into the HVGO acid-only fraction indicating that the fractionation is not selective for neutral nitrogen compounds, as expected. N$_1$ species in the acid-free fraction have slightly higher DBE values and carbon numbers than for the HVGO. These species are in the HVGO fraction, but are masked by the O$_2$ carboxylic acids that are ionized more efficiently than pyrrolic nitrogen. However, removal of the O$_2$ species by Acid-IER fractionation does enable identification of species in low relative abundance in the original bitumen.

In summary, negative-ion electrospray FT-ICR MS allows for selective ionization of polar acidic species of Athabasca Canadian bitumen and its IER isolated HVGO acid-only and acid-free fractions. The ultrahigh resolution and mass accuracy of FT-ICR MS, combined with Kendrick mass sorting, enable the assignment of unique elemental compositions to all above-threshold mass spectral peaks. Most naphthenic acids (O$_2$ and S$_1$O$_2$ classes) in the raw bitumen distill into the HVGO but with truncated DBE and carbon number distributions due to the boiling point constraints of the HVGO fraction.

Comparison of the class, type and carbon number distributions of the raw bitumen, HVGO and HVGO acid-only fraction indicates that naphthenic acid (O$_2$ class) content can be determined from the raw bitumen alone, so that IER fractionation does not yield new information about the acid composition. However, the acid-IER fractionation increases the relative abundance of species in the acid-free fraction, due
to removal of O$_2$ components, and thus improves N$_1$ speciation. In addition, IER may preferentially concentrate short-chain naphthenic acids. The elution of S$_1$O$_2$ species in the acid-only fraction suggests they are most likely thiophene-based carboxylic acids. The presence of higher S$_X$O$_X$ classes in the acid-free fraction (not observed in the raw bitumen or HVGO) suggests that they are non-naphthenic acid in character.
CHAPTER 4.

CHARACTERIZATION OF ATHABASCA BITUMEN HEAVY VACUUM GAS OIL DISTILLATION CUTS BY NEGATIVE/POSITIVE ELECTROSPRAY IONIZATION AND AUTOMATED LIQUID INJECTION FIELD DESORPTION IONIZATION FT-ICR MS

Summary

We have analyzed eight heavy vacuum gas oil (HVGO) distillation fractions, IBP-343 °C, 343-375 °C, 375-400 °C, 400-425 °C, 425-450 °C, 450-475 °C, 475-500 °C and 500-525 °C, of Athabasca bitumen by Fourier transform ion cyclotron mass spectrometry. Acidic, basic, and non-polar components were detected by negative-ion and positive-ion electrospray ionization (ESI) and automated liquid injection field desorption (FD) ionization positive-ion FT-ICR MS. Ultrahigh mass resolving power (m/Δm_{50%} ≈ 350,000) and high mass accuracy (< 500 ppb) facilitate the assignment of a unique elemental composition to each peak in the mass spectrum. Thus, each distillate was characterized by mass, heteroatom class, type (number of rings and double bonds), and carbon number distribution to correlate compositional changes with increased boiling point. Negative-ion ESI FT-ICR MS identifies high relative abundance non-aromatic O₂ species that span the entire distillation range. All ionization methods reveal an increase in double-bond equivalents (DBE, the number of rings plus double bonds) and carbon number with increased distillation temperature. In addition, some structural information can be inferred from increases in DBE value with increased distillation temperature. Summed data for individual distillation cuts yield class specific isoabundance contours similar to that for the feed HVGO, suggesting that class-specific carbon number and DBE distributions for individual distillation cuts could be estimated from the high-resolution feed HVGO mass spectrum.
Introduction

The current production of bitumen from oil sands in Alberta is close to 1.2 million barrels per day and is expected to reach 5-6 million barrel per day by the year 2030. The non-ideal bulk properties of bitumen/heavy oils, such as high viscosity, density, and sulfur create challenges and opportunities for the transportation and processing of these commodities. For example, diluent (up to 30 vol%) is required to reduce the viscosity so that the bitumen meets pipeline specifications. Bitumen also presents production/process issues related to minor components such as clays, metals, salts and acids. Oil sands expansion in northern Alberta currently focuses on mining techniques but future developments for bitumen production will be based on in situ techniques such as steam assisted gravity drainage (SAGD) and other methods such as vapor extraction (VAPEX) and toe-to-heel air injection (THAI™) processes. The variation in minor components according to production method is important given the vastness of the reserve, and is currently the subject of investigation at the National Centre for Upgrading Technology (NCUT).

Organic acids in petroleum have been characterized extensively by a variety of techniques, including FT-IR spectroscopy, 13C NMR, gas chromatography (GC) based methods such as GC-MS and GCxGC, and mass spectrometry with various ionization sources including fast-atom bombardment (FAB), chemical ionization (CI), and electrospray ionization (ESI). Recently a number of investigations have focused on the naphthenic acids in Alberta bitumens. Although Athabasca bitumen has a high total acid number (TAN = 3.5-5.0 mg KOH/g oil), its corrosivity in oil sand processing plants has not been reported. In a recent investigation by the members of Canadian Crude Quality Technical Association (CCQTA), the corrosivity of the gas oil fraction of Athabasca bitumen was
found to be lower than that for a known corrosive gas oil based on the spinning cage technique.\textsuperscript{111} The low corrosivity of Athabasca bitumen, like other crude oils, can be attributed in part to its high sulfur content.\textsuperscript{82}

It has been suggested that the naphthenic acids present in Athabasca bitumen have a bimodal molecular weight distribution. The larger “β” naphthenic acids are said to be sterically hindered and cannot interact with a metal surface effectively to cause corrosion.\textsuperscript{110} However, we have recently shown that acidic species in crude oil and Athabasca bitumen easily self-associate to form multimers in a bimodal distribution.\textsuperscript{109} Moreover, Gray et. al. have shown that naphthenic acids from a heavy vacuum gas oil (HVGO) fraction of Athabasca bitumen have different reactivity with iron powder; ESI FT-ICR MS showed that the higher molecular naphthenic acids are more reactive with the iron.\textsuperscript{112}

In the late 1960’s, Snyder extensively characterized the 400-700 °F (204-371 °C) and 850-1000 °F (454-538 °C) fractions of a California crude oil by IR, UV and low voltage electron ionization (EI) high resolution mass spectrometry.\textsuperscript{116, 117} Boduszynski et al. released a series of papers on the relation of molecular composition of heavy petroleum to boiling point.\textsuperscript{7-10} Middle distillates have been characterized by supercritical fluid chromatography coupled to time-of-flight (TOF) mass spectrometry,\textsuperscript{118} chemical ionization high-resolution mass spectrometry, and simultaneous orthogonal acceleration TOF-magnet scanning tandem mass spectrometry,\textsuperscript{119}, and GCxGC.\textsuperscript{120} In addition, high-boiling distillates have been characterized by high performance liquid chromatography with refractive index and ultraviolet detection\textsuperscript{121} as well as 1H and 13C NMR.\textsuperscript{121, 122} ESI and low-voltage EI FT-ICR MS have been used to characterize the acidic, basic and non-polar species in three distillation cuts (295-319 °C, 319-456 °C and 456-543°C) of a vacuum gas oil from a high TAN, low sulfur crude oil.\textsuperscript{123, 124} Low-voltage EI and ESI show an increase in molecular weight, heteroatom containing
classes, DBE and extent of alkylation with increased distillation temperature. However, the broad distillation temperature ranges show overlap in chemical speciation. In addition, the low sulfur content of the crude oil does not allow extensive speciation of organic or non-polar sulfur over the distillation range.

Here we have fractionated a HVGO of Athabasca bitumen into 8 fractions by vacuum distillation and analyzed the components by negative/positive-ion ESI FT-ICR MS and automated liquid injection field desorption (FD) ionization positive-ion FT-ICR MS. The main objectives were to investigate the evolution of acidic species under standard distillation conditions and to determine whether these species undergo any structural changes as a function of temperature. In addition, the compositional changes of basic and non-polar species through the distillation process may be monitored by positive-ion ESI and FD FT-ICR MS.

**Experimental Methods**

**Sample Description and Preparation for ESI MS**

A heavy gas oil fraction from Athabasca Canadian bitumen was fractionated into 8 fractions by ASTM D-1160. Distillate fractions were collected in 25°C intervals and the last fraction (500-525 °C) constitutes the material left in the pot after the 475-500 °C fraction was collected. The boiling point distribution of each fraction was determined by high temperature small-scale distillation and the TAN was measured by ASTM D-664. The sulfur and nitrogen contents of the fractions were measured by ASTM D-4294 and ASTM D-4629. Oxygen content was determined by the Unterzaucher method. Bulk molecular weight was determined by vapor pressure osmometry (VPO) with toluene as the solvent (ASTM D-2503).
Bitumen HVGO distillation cuts for ESI FT-ICR MS were diluted to 1 mg/mL in 50:50 (v/v) toluene:methanol. To ensure efficient protonation/deprotonation, 1 µL of acetic acid/ammonium hydroxide was added per 100 mL of sample solution (~ 65 fM). Sample solutions were analyzed without additional treatment. Bitumen samples for automated LIFDI were diluted to 100 µg/mL in methylene chloride and analyzed without additional treatment.

**Instrumentation: Electrospray FT-ICR MS**

All electrospray FT-ICR MS experiments were performed on the 9.4 T ESI FT-ICR mass spectrometer described in Chapter 1.

**Instrumentation: Automated LIFDI FT-ICR MS**

All automated LIFDI FT-ICR MS experiments were performed on the 9.4 T FD FT-ICR mass spectrometer described in Chapter 2.

**Mass Calibration and Data Analysis**

Negative-ion electrospray ESI FT-ICR mass spectra were internally calibrated\(^1\)\(^,\)\(^2\) with respect to a homologous series containing two oxygen atoms (3 DBE) present in high relative abundance in each sample.\(^74\) Similarly, positive-ion electrospray FT-ICR MS mass spectra were internally calibrated with respect to a homologous series containing one nitrogen atom (9 DBE). Automated LIFDI FT-ICR MS spectra were calibrated with respect to a high abundance hydrocarbon homologous series (4 DBE) in each sample. Singly-charged ions (200 < m/z < 1200) with relative abundance greater than eight standard deviations of baseline noise (8σ) were exported to a spreadsheet. Measured masses were converted from the IUPAC mass scale to the Kendrick mass scale\(^19\).
for easier identification of homologous series. Peaks were assigned by Kendrick mass defect analysis as previously described.$^{20}$

**Results and Discussion**

The high complexity of petroleum samples requires ultrahigh resolution to resolve each peak in the mass spectrum. The analysis of narrow distillation cuts decreases the complexity of the mass spectrum; however ultrahigh resolution is still required to resolve closely spaced peaks, such as the 3.4 mDa split (C$_3$ vs. SH$_4$) throughout the mass spectrum. Figure 4.1 shows a 500-525 °C distillation cut of Athabasca bitumen HVGO, with >3,700 assigned peaks (> 8σ of baseline noise) from 300-800 Da, with a mass resolving power (m/Δm$_{50\%}$) greater than 450,000 at m/z=500, sufficient to resolve the 3.4 mDa split (see inset in Figure 1). Due to the large number of peaks per spectrum (here, 1,300 to 4,600), we employ heteroatom class analysis (i.e., molecules with a common number of N, O, and S atoms) and color-coded isoabundance plots of double bond equivalents (DBE, the number of rings and or double bonds) versus number of carbons to simplify data interpretation. Contour plot images allow large amounts of data to be viewed in a compact form and easily compared with other samples.$^{20}$
Figure 4.1: Broadband negative-ion ESI FT-ICR mass spectrum of a 500-525 °C distillation cut from Athabasca Canadian bitumen, at 1 mg/mL. The mass scale-expanded inset illustrates the need for ultrahigh resolution for petroleum samples to resolve ions whose elemental composition differs by, e.g., C₃ vs. SH₄ (3.4 mDa).

The vacuum gas oil was flash distilled (ASTM D-1160), resulting in some overlap between species in different fractions (see Figure 4.2). However, good distillate recovery (0.28 wt% loss) was achieved. Table 4.1 lists properties for the HVGO distillate fractions. The heteroatom (N, S and O) content increases with increased boiling point, as also seen in multi-heteroatom containing classes from the ESI FT-ICR MS (see Figs. 4.3 and 4.6). High sulfur content is observed in the field desorption ionization derived class analysis (see Fig. 4.9) as a prominent S₁ class. Similarly, high oxygen content is observed in the negative-ion ESI FT-ICR MS derived class analysis (see Fig. 4.3) distributed over a wide range of
oxygen containing classes. Molecular weight (by vapor phase osmometry) increases with increased cut temperature range and is also observed by FT-ICR MS as an increase in carbon number (see Figs. 3-8). The increase in TAN with increased boiling point suggests that naphthenic acids are present in the high boiling distillates.

Table 4.1: Properties of Athabasca Bitumen HVGO Distillation Fractions

<table>
<thead>
<tr>
<th>Fraction (°C)</th>
<th>IBP-343</th>
<th>343-375</th>
<th>375-400</th>
<th>400-425</th>
<th>425-450</th>
<th>450-475</th>
<th>475-500</th>
<th>500-525</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight % Distilled</td>
<td>4.32</td>
<td>15.87</td>
<td>17.13</td>
<td>9.87</td>
<td>18.91</td>
<td>17.02</td>
<td>9.13</td>
<td>7.47</td>
</tr>
<tr>
<td>Density (g/mL, @ 15.6 °C)</td>
<td>0.9224</td>
<td>0.9348</td>
<td>0.9684</td>
<td>0.9664</td>
<td>0.9706</td>
<td>0.9762</td>
<td>0.9788</td>
<td>0.9940</td>
</tr>
<tr>
<td>Carbon (wt %)</td>
<td>85.68</td>
<td>84.76</td>
<td>84.19</td>
<td>84.20</td>
<td>84.24</td>
<td>83.96</td>
<td>85.20</td>
<td>64.70</td>
</tr>
<tr>
<td>Hydrogen (wt %)</td>
<td>11.37</td>
<td>10.98</td>
<td>11.40</td>
<td>11.38</td>
<td>10.97</td>
<td>10.80</td>
<td>10.84</td>
<td>10.24</td>
</tr>
<tr>
<td>Nitrogen (ppm)</td>
<td>301.6</td>
<td>584.0</td>
<td>941.2</td>
<td>1211</td>
<td>1441</td>
<td>1791</td>
<td>1600</td>
<td>2600</td>
</tr>
<tr>
<td>Sulfur (wt %)</td>
<td>2.33</td>
<td>3.02</td>
<td>3.30</td>
<td>3.42</td>
<td>3.77</td>
<td>3.44</td>
<td>3.80</td>
<td>4.29</td>
</tr>
<tr>
<td>Oxygen (wt %)</td>
<td>0.86</td>
<td>1.14</td>
<td>1.14</td>
<td>1.28</td>
<td>1.34</td>
<td>1.36</td>
<td>1.5</td>
<td>1.71</td>
</tr>
<tr>
<td>Molecular Weight, VPO (g/mol)</td>
<td>288</td>
<td>287</td>
<td>304</td>
<td>326</td>
<td>359</td>
<td>402</td>
<td>461</td>
<td>578</td>
</tr>
<tr>
<td>TAN (mg KOH/g oil)</td>
<td>1.14</td>
<td>2.35</td>
<td>3.49</td>
<td>4.24</td>
<td>4.74</td>
<td>5.32</td>
<td>5.61</td>
<td>5.06</td>
</tr>
</tbody>
</table>

Figure 4.2: Percentage (by weight) lost as a function of temperature for each of eight distillate fractions of Athabasca bitumen HVGO derived from simulated distillation. Note the overlap in boiling points for components from different distillate fractions.
The negative-ion ESI class analyses (heteroatom content) (see Figure 4.3) are consistent with class analyses previously reported for Athabasca bitumen and Athabasca bitumen HVGO (see Chapter 3).

The O₂ class (presumably naphthenic acids) has the highest relative abundance in each sample, followed by the S₁O₂ class. The O₂ class relative abundance decreases with increased cut temperature range, likely due to the increase in multi-heteroatom containing classes (O₂+x, NₓOₓ and SₓOₓ) with increasing cut temperature range. This increase in multi-heteroatom classes agrees well with the bulk analyses which also show an increase in nitrogen, oxygen and sulfur (by weight) with
increasing cut temperature range. We are currently attempting to identify the $S_xO_x$ and $O_{2+x}$ species observed by negative-ion ESI FT-ICR MS.

Isoabundance contours for a plot of DBE versus the carbon number for the $O_2$ class are shown in Figure 4.4. Relative abundance is scaled to the highest relative abundance $O_2$ peak from all eight distillation cuts. Increase in distillation temperature is accompanied by a shift in the carbon number distribution from 18-31 for the IBP-343 °C cut to 34-44 for the 500-525 °C cut. However, the species with highest relative abundance in each sample remain at a DBE of 3. Due to similarity between compositions for the middle boiling point ranges, subsequent isoabundance contour plots will show only the IBP-343 °C, 375-400 °C, 475-500 °C and 500-525 °C cuts.

Figure 4.5 shows isoabundance contours for a plot of DBE versus the carbon number for the $S_1O_2$ class. The 475-500 °C cut has the highest relative abundance of $S_1O_2$ species. The carbon number distribution again shifts to higher carbon number with increasing cut temperature range, from ~17-32 for the IBP-343 °C cut to 27-42 for the 500-525 °C cut. The bimodal DBE distribution suggests two stable core structures. The high relative abundance components near DBE 4 are consistent with a core structure of a thiophenic ring with an attached carboxylic acid group (possible structure shown in Figure 4.5 top right), whereas the more aromatic species near DBE 7 are consistent with a core structure of a benzothiophenic ring with a carboxylic acid attached (see Figure 4.5 bottom left for possible structure). Proposed structures should include alkyl chains to account for additional carbon and hydrogen. A similar bimodal distribution is seen for the $S_2O_2$ class (data not shown).
Figure 4.4: Color-coded isoabundance contours for plots of double-bond equivalents (DBE) versus the carbon number for the O_2 class for all cuts derived from negative-ion ESI FT-ICR mass spectra.
Figure 4.5: Isoabundance contours for plots of double-bond equivalents (DBE) versus the carbon number for the $S_1O_2$ class derived from negative-ion ESI FT-ICR mass spectra. Top left, IBP-343 °C; top right, 375-400 °C; bottom left, 475 – 500 °C; and bottom right, 500-525 °C cuts. Possible representative core structures are shown for DBE 4 (top right) and DBE 7 (bottom left).

**Positive-Ion ESI FT-ICR MS**

Selected basic heteroatom containing classes for 5 distillation cuts are shown in Figure 4.6 for positive-ion ESI FT-ICR MS. The N$_1$ class has the highest relative abundance for each cut. Multi-heteroatom containing classes ($N_2$, $N_1S_2$, $N_1O_1$ and $N_2O_2$) increase in abundance with an increase in cut temperature range. Again, the increase in multi-heteroatom classes agrees well with the bulk analyses that show an increase in nitrogen, oxygen and sulfur (by weight) with increasing distillation temperature range. The N$_1$ class decreases in relative
abundance, presumably due to increased relative abundance of multi-heteroatom containing species.

Figure 4.6: Heteroatom class distribution (heteroatom content) for Athabasca bitumen HVGO distillation cuts derived from positive-ion ESI FT-ICR mass spectra.

Isoabundance contours for a plot of DBE versus the carbon number for the basic N$_1$ containing species are shown in Figure 4.7. As for the negative-ion ESI data, the carbon number distribution shifts higher with increasing cut temperature range: from 21-32 for the IBP-343 °C cut to 35-43 for the 500-525 °C cut. In addition, the most abundant N$_1$ class species also shift to higher DBE with an increase in boiling point: from DBE 7 N$_1$ for the IBP-343 °C and 375-400 °C cuts, consistent with a possible quinoline-like core structure (see Figure 5 top right) to DBE 9 for the 475-500 °C and 500-525 °C cuts, consistent with a possible acridine-like core structure (see Figure 5 bottom left). Similar
carbon number and DBE trends are seen in the N$_1$S$_1$ class, as shown in **Figure 4.8**. Surprisingly, the species of highest relative abundance have the same DBE values as the N$_1$ class (DBE 7 and 10). If the sulfur were in a thiophenic ring, there would be an increase of 2 DBE from the N$_1$ core structure, suggesting that the sulfur may exist in a thioether form. However, the most abundant N$_1$S$_2$ species have DBE 9 and 12, consistent with the addition of a thiophenic ring (2 additional DBE) to the aromatic core of the DBE 7 and 10 N$_1$S$_1$ class (data not shown).

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**Figure 4.7**: Isoabundance contours for plots of double-bond equivalents (DBE) versus the carbon number for the N$_1$ class for selected cuts derived from positive-ion ESI FT-ICR mass spectra. Top left, IBP-343 °C; top right, 375-400 °C; bottom left, 475-500 °C; and bottom right, 500-525 °C cuts. Possible representative core structures are shown for DBE 7 (top right) and DBE 10 (bottom left).
Figure 4.8: Isoabundance contours for plots of double-bond equivalents (DBE) versus the carbon number for the $N_1S_1$ class for selected cuts derived from positive-ion ESI FT-ICR mass spectra. Top left, IBP-343 °C; top right, 375-400 °C; bottom left, 475 – 500 °C; and bottom right, 500-525 °C cuts.

Automated LIFDI FT-ICR MS

Class distributions (heteroatom content) derived from automated positive-ion LIFDI FT-ICR MS show the hydrocarbon class with the highest relative abundance for each cut, followed by the $S_1$, $S_2$, $N_1$ and $O_1$ classes (Figure 4.9). An increased cut temperature range yields a decrease in $N_1$ and $O_1$ species. Sulfur-containing species are more abundant in the lower-boiling cuts (IBP-343 and 375-400 °C) whereas hydrocarbons are more abundant in the higher-boiling cuts (475-500 °C and 500-525 °C).
Figure 4.9: Heteroatom class distribution (heteroatom content) for Athabasca bitumen HVGO distillation cuts derived from automated LIFDI positive-ion FT-ICR mass spectra.

Isoabundance contours for a plot of DBE versus carbon number for the hydrocarbon class are shown in Figure 4.10. The hydrocarbon class is most abundant in the IBP-343 °C cut, with the most abundant species at DBE 2 (i.e., non-aromatic). The carbon number distribution increases and broadens with increased cut temperature range, from ~18-28 for IBP-343 °C ~35-50 for the 500-525 °C cut. However, the aromaticity of hydrocarbon species changes little for higher-temperature cuts, with a range of DBE ~2-8 across all four cuts.
Figure 4.10: Isoabundance contours for plots of double-bond equivalents (DBE) versus the carbon number for the hydrocarbon class for selected cuts derived from automated LIFDI positive-ion FT-ICR mass spectra. Top left, IBP-343 °C; top right, 375-400 °C; bottom left, 475 – 500 °C; and bottom right, 500-525 °C cuts.

**Figure 4.11** shows isoabundance contours for a plot of DBE versus carbon number for the $S_1$ class. The most abundant $S_1$ species (DBE 6) are found in the IBP-343 °C cut, consistent with a benzothiophene core structure of (see Figure 4.11, top left for representative structure). The areas of high relative abundance at DBE 3 and 9 are consistent with possible core structures of a thiophenic ring and dibenzothiophenic ring systems (see Figure 4.11 top left and top right for representative structures). The carbon number distribution again increases with increasing cut point temperature range, from ~16-26 for the IBP-323 °C cut to ~33-44 for the 500-525 °C cut. The aromaticity again changes little with increased cut point temperature range, averaging DBE ~6 for every cut.
Figure 4.11: Isoabundance contours for plots of double-bond equivalents (DBE) versus the carbon number for the S<sub>1</sub> class for selected cuts derived from automated LIFDI positive-ion FT-ICR mass spectra. Top left, IBP-343 °C; top right, 375-400 °C; bottom left, 475-500 °C; and bottom right, 500-525 °C cuts. Possible representative core structures are shown for DBE 3 and 6 (top left) and DBE 9 (top right).

Unlike ESI, LIFDI generates ions from hydrocarbons and thiophene-containing molecules. However, LIFDI yields narrower carbon number and DBE distributions than from ESI analysis of the same samples. Moreover, LIFDI is a pulsed ionization source (unlike the continuous ionization provided by ESI and atmospheric pressure photoionization (APPI), and thereby requires much more time to acquire data. Fragile FD emitters can easily break and can become overloaded with sample and/or residue after a large number of sample doses, and replacement of the FD emitter requires a time-consuming break in source chamber vacuum. Finally, LIFDI FT-ICR MS experiments typically yield lower DBE coverage (DBE 0-20 than APPI (DBE 0-35),...
which also targets hydrocarbons and non-polar sulfur. For the above reasons, we now prefer APPI for analysis of hydrocarbons and non-polar sulfur species in hydrocarbon-containing samples.\textsuperscript{38}

**Structural Changes as a Function of Boiling Point**

Figures 4.4, 4.5, 4.7, 4.8, 4.10 and 4.11 show that the increase in carbon number and DBE distributions is continuous and gradual across the distillation temperature range.\textsuperscript{114} Since correlations between boiling point and molecular structure are well known\textsuperscript{7, 8, 42}, the estimation of C\# and DBE distributions for a given or series of distillation cuts should be possible from a broadband FT-ICR mass spectrum of the feedstock. **Figure 4.12** shows close agreement between the isoabundance contours for plots of DBE versus the carbon number for the HVGO feed (Fig. 4.12 left) and for summed data for the analyzed distillation cuts (Fig. 4.12 right) for the O\textsubscript{2} class (negative-ion ESI, top) and the N\textsubscript{1} class (positive-ion ESI, bottom). The detailed compositional information derived from FT-ICR MS can determine DBE and carbon number distributions for all species in the mass spectrum, and thus the boiling point range of those species can be estimated. The summed contours show minor variations in DBE and carbon number ranges compared to that of the HVGO feed due to dynamic range limitations of broadband FT-ICR MS analysis, a potential problem for similar analysis of heavier petroleum feedstocks.

**Conclusions**

We have applied positive- and negative-ion ESI and LIFDI positive-ion FT-ICR MS for detailed compositional characterization of Athabasca bitumen HVGO distillate fractions. Increased molecular weight, DBE, and extent of alkylation are observed with increased distillation temperature, and agree well with prior FT-ICR MS analyses.\textsuperscript{123, 124} In addition, the number of heteroatom-containing classes from negative-
Figure 4.12: Isoabundance contours for plots of double-bond equivalents (DBE) versus the carbon number for the O₂ class (top) derived from negative-ion ESI FT-ICR mass spectra and the N₁ class (bottom) derived from positive-ion ESI FT-ICR mass spectra. The contours on the left are for the HVGO feed and those on the left are for the sum-of all analyzed distillation cuts.
and positive-ion ESI increase with an increase in boiling point, in accord with bulk measurements.

Non-aromatic $O_2$ species (DBE 3) persist throughout the distillation process and fractionate according to aggregate alkyl chain length. Acidic sulfur-containing classes ($S_1O_2$, $S_2O_2$) exhibit a bimodal DBE distribution, suggesting two stable core structures, with the higher DBE structures favored at higher distillation temperature. Non-polar hydrocarbons and sulfur, detected by automated LIFDI FT-ICR MS, exhibit the same trends of increased DBE and alkylation with increased distillation temperature. Non-polar sulfur for the $S_1$ class has a trimodal distribution at DBE values corresponding to thiophene-based core structures.

ESI and automated LIFDI FT-ICR MS can rapidly and reproducibly monitor the compositional changes of polar and non-polar heteroatomic species in HVGO from Athabasca bitumen. These methods can be applied to the entire range of petroleum distillates with small sample consumption and selective ionization for the species of interest. FT-ICR MS facilitates observation of thousands of species in each mass spectrum simultaneously, as well as their molecular weight, heteroatom content, DBE (aromaticity) and extent of alkylation (carbon number distribution). The summation of distillation cuts yields isoabundance contour plots similar to those derived from broadband FT-MS of the HVGO feed, suggesting that speciation of individual distillation cuts can be estimated from broadband mass spectra of the whole feedstock.
CHAPTER 5.

ANALYSIS OF ACIDIC SPECIES IN THERMALLY TREATED ATHABASCA BITUMEN BY NEGATIVE-ION ELECTROSPRAY FT-ICR MASS SPECTROMETRY

Summary

We examine molecular transformations of thermally treated Athabasca bitumen heavy vacuum gas oil (HVGO) by ultra-high resolution negative-ion electrospray Fourier transform ion cyclotron resonance mass spectrometry. HVGOs treated at temperatures of 300, 325, 350 and 400 °C were characterized by class (hetero-atom content), type (number of rings plus double bonds) and carbon number distribution. In addition, the inert helium sweep gas of the autoclave was collected, condensed and analyzed. The total acid number (TAN) of the HVGOs decreases with increasing treatment temperature. The O_2 class contains high relative abundance of species with three double bond equivalents (DBE, number of rings plus double bonds), but no compositional changes occur with increased treatment temperature. A bimodal distribution is observed for the S_1O_2 class, indicative of two possible stable core structures. Low relative abundance classes show only small changes with thermal treatment. Condensed helium sweep gas contains high relative abundance of low carbon number O_2 species with DBE of 3. The S_1O_2 class displays the same bi-modal distribution as the HVGOs, but at lower carbon number than the parent HVGOs. The similarity of the O_2 speciation upon thermal treatment and acids present in the inert sweep gas suggest the decrease in TAN is due to boil-off and subsequent loss of the lower carbon number acids formed, rather than thermal transformation of naphthenic acids.
Introduction

The oil sand deposits in Alberta, Canada the second largest reserve of recoverable crude oil, estimated at 175 billion barrels. The low API gravity (7-15°) and high heteroatom content (nitrogen, sulfur, oxygen, NSO) of recovered bitumen creates transportation and refining challenges for these feedstocks. In particular, the organic acids, also known as naphthenic acids, are of considerable interest due to their role in refinery corrosion, termed naphthenic acid corrosion. Feedstocks with a total acid number (mg of KOH needed to neutralize one gram of crude oil, TAN) > 0.5 and side-streams with TAN >1.5 are considered unsuitable for processing in typical refineries. However, industry experience shows that while TAN may be a good indicator of whether a crude oil may be corrosive, it is not necessarily useful to determine the severity of expected corrosion. In addition, Athabasca bitumen has a TAN of ~3.2-5.5, well above the established limit, but reports on refinery corrosion due to naphthenic acids in oil sands processing is limited.

Naphthenic acid corrosion commonly occurs in atmospheric distillation towers where the crude oil and distillation temperatures are between 220 and 400 °C. However, there is little information on the thermal stability of naphthenic acids at these temperatures. Corrosive feeds in this distillation range have been found to contain low molecular weight (160-350 m/z), low DBE organic acids by negative-ion fast-atom bombardment mass spectrometry. In addition, petroleum acids as a whole have been characterized by a number of methods, including FT-IR spectroscopy, 13C NMR, two dimensional gas chromatography, gas chromatography-mass spectrometry and liquid-secondary ion mass spectrometry. Mass spectrometry with various ionization sources has also been used, such as fast atom bombardment, chemical ionization, atmospheric pressure chemical ionization and electrospray ionization (ESI).
Here we report the results of thermal conversion of an Athabasca bitumen heavy vacuum gas oil (HVGO, 350-525 °C) in order to determine the thermal stability of bitumen HVGO acids. Thermal treatment was performed between temperatures of 300 and 400 °C and the liquid products and condensed sweep gas products were analyzed by various bulk analyses and negative-ion ESI FT-ICR MS. Bulk TAN analysis indicates a decrease in TAN at higher treatment temperature. The ultrahigh mass resolving power \( (m/\Delta m_{50\%} > 350\ 000) \) and high mass accuracy (better than 500 ppb) of FT-ICR MS allow for the assignment of a unique elemental composition to each peak in the mass spectrum.\(^3\) Thus, the elemental composition assignment allows for the organization of compounds by class (heteroatom content), type (double-bond equivalents [DBE], the number of rings and/or double bonds], and carbon number. Therefore, the ESI FT-ICR MS results identify polar organic acids that are resistant to thermal treatment, and those that may be responsible for the decrease in TAN at higher treatment temperatures.

**Experimental Methods**

**Sample Description and Bulk Measurements**

Heavy vacuum gas oil (HVGO) was obtained from Athabasca bitumen, approximately 30 wt% with a boiling range of 350-525 °C (ASTM D1160 distillation).\(^9\) TAN was measured by the ASTM D-664 method. Water content was determined by Karl Fischer titration. Bulk molecular weight was determined by vapor pressure osmometry at 120°C in o-dichlorobenzene at 130°C.
Thermal Treatment

HVGO thermal treatment experiments were carried out in a 1-L stirred tank autoclave at reaction temperatures of 300, 325, 350 and 400 °C at 100 PSI for 60 minutes residence time. A continuous flow of nitrogen at 30 mL/min was used to remove any water from decarboxylation reactions and to prevent reverse reactions. Major liquid products from the reactor, light ends from the condenser and gaseous products were collected for analysis.

Sample Preparation for ESI FT-ICR MS

Bitumen samples were dissolved in 50:50 (v/v) toluene:methanol solvent to a concentration of 1 mg/mL. Ammonium hydroxide was added (10 µL to every 1 mL of sample solution, ~65 fM) to ensure efficient ionization (deprotonization) for negative-ion electrospray analysis. All solvents were HPLC grade (Fisher Scientific, Pittsburgh, PA).

Instrumentation

All electrospray FT-ICR MS experiments were performed on the 9.4 T ESI FT-ICR mass spectrometer described in Chapter 1.

Mass Calibration and Data Analysis for ESI FT-ICR MS

FT-ICR mass spectra were internally calibrated\textsuperscript{1,2} with respect to a high abundance homologous series of ions each containing two oxygen atoms.\textsuperscript{74} The mass values (for singly charged ions) of 250 - 1000 Da with a relative abundance greater than six times the standard deviation of the baseline noise were exported to a spreadsheet. Measured masses were converted to the Kendrick mass scale\textsuperscript{19} and sorted by Kendrick mass
defect values to facilitate identification of homologous series and peak assignments as previously described.\(^{20}\)

**Results and Discussion**

**Bulk Properties of HVGO Feed and Treatment Products**

Properties of the HVGO feed, thermal treatment liquid products and condenser products are shown in Table 5.1.

Table 5.1: Properties of HVGO Feed, Treatment Liquid Products and Condenser Products

<table>
<thead>
<tr>
<th></th>
<th>HVGO (feed)</th>
<th>300 °C</th>
<th>325 °C</th>
<th>350 °C</th>
<th>400 °C</th>
<th>350 °C</th>
<th>400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Analysis, wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>85.33</td>
<td>84.72</td>
<td>84.53</td>
<td>84.75</td>
<td>84.91</td>
<td>84.20</td>
<td>83.8</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>10.44</td>
<td>11.20</td>
<td>11.42</td>
<td>11.40</td>
<td>11.36</td>
<td>12.00</td>
<td>13.20</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.14</td>
<td>0.21</td>
<td>0.22</td>
<td>0.21</td>
<td>0.24</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3.48</td>
<td>3.40</td>
<td>3.51</td>
<td>3.56</td>
<td>3.32</td>
<td>2.74</td>
<td>2.23</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.83</td>
<td>0.93</td>
<td>0.94</td>
<td>0.92</td>
<td>0.83</td>
<td>0.94</td>
<td>0.91</td>
</tr>
<tr>
<td>TAN (mg KOH/g oil)</td>
<td>4.32</td>
<td>4.13</td>
<td>3.89</td>
<td>3.58</td>
<td>1.46</td>
<td>3.93</td>
<td>5.76</td>
</tr>
<tr>
<td>Molecular Weight (VPO, g/mol)</td>
<td>345</td>
<td>333</td>
<td>338</td>
<td>337</td>
<td>343</td>
<td>422</td>
<td>723</td>
</tr>
<tr>
<td>Liquid Recovery (wt%)</td>
<td>99.07</td>
<td>99.49</td>
<td>99.40</td>
<td>96.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Condenser Recovery (wt%)</td>
<td>0.097</td>
<td>0.122</td>
<td>0.970</td>
<td>6.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water (Kf, wt%)</td>
<td>0.048</td>
<td>0.040</td>
<td>0.034</td>
<td>0.035</td>
<td>0.13</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>Gaseous Products (wt%)</td>
<td>0.221</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Recovery (wt%)</td>
<td>99.21</td>
<td>99.65</td>
<td>100.4</td>
<td>102.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{4}\) negligible gaseous products recovered

The elemental analyses are very similar over the treatment temperature range, with a slight decrease in oxygen content at 400 °C. The condenser products have a higher wt% of hydrogen, and thus a lower H/C ratio, which suggests less aromatic species than the treatment liquid products. TAN number slowly decreases up to 400 °C, where it drops dramatically to 1.46. The condenser products have very high TAN numbers, an indication that acids are carried into the condenser by the sweep gas. The molecular weights (by VPO) of the HVGO feed and liquid
products are all very similar, between 330-345 g/mol. However, the condenser products have higher molecular weights, especially the 400 °C condenser sample, with a molecular weight greater than 2x that of the HVGO. This anomalous molecular weight can be explained as solution aggregates of acidic species in the VPO solvent. Good material balances were obtained for all reactions, with very few gaseous products formed. The major liquid products contained little water, but the condenser products contained more water as expected. Simulated distillation of the HVGO feed and the major liquid products from thermal treatment are shown in Figure 5.1.

![Simulated Distillation of Thermal Treatment Liquid Products](image)

Figure 5.1: Percentage (by weight) lost as a function of temperature for the major liquid products collected from the autoclave for thermally treated Athabasca bitumen HVGO derived from simulated distillation. Low-boiling species are produced at the 400 °C treatment temperature.

There is little change in the boiling point distribution until the 400 °C treatment temperature, where lower boiling point products are formed.
The similarity of the bulk analyses prompted the analyses of the samples by ultra-high resolution ESI FT-ICR MS to assess changes in the chemical composition of polar acidic species after thermal treatment.

**Negative-Ion ESI FT-ICR MS**

Figure 5.2 shows broadband negative ion ESI FT-ICR mass spectra of the HVGO feed.

Figure 5.2: Broadband negative-ion ESI FT-ICR mass spectra of Athabasca bitumen heavy vacuum gas oil. The mass scale-expanded inset highlights a mass difference of 3.4 mDa, which is resolved over the entire mass range only with the ultra-high mass resolving power of FT-ICR MS.

The inset illustrates the need for ultra-high resolution across the entire mass range (300 > m/z > 1 000); isobaric compounds, such as those with elemental compositions of C₃ versus S₁H₄ (3.4 mDa) require a mass
resolving power greater than $m/\Delta m_{50\%} = 147000$ (where $m$ is the ion mass and $\Delta m_{50\%}$ is the full spectra width at half-height) to resolve these signals at $m/z=500$.

All thermal treatment liquid products display the same mass range ($m/z$ 300-700) (data not shown). The class analysis (heteroatom content) for the HVGO feed and thermal treatment liquid products are shown in Figure 5.3.

![Thermally Treated Athabasca Bitumen HVGO Negative-Ion ESI FT-ICR MS Class Analysis](image)

Figure 5.3: Heteroatom class distribution (heteroatom content) for Athabasca bitumen HVGO feed and thermal treatment liquid products derived from negative-ion ESI FT-ICR mass spectra. Inset shows the $N_1O_2$, $S_1O_4$ and $O_4$ classes in more detail.

The $O_2$ class, presumably naphthenic acids, has the highest relative abundance in each sample, followed by the $S_1O_2$ class. The HVGO has the highest relative abundance of $O_2$ species, and the thermally treated samples show approximately the same relative abundance over the treatment temperature range. The $S_1O_2$ class shows similar relative
abundance for the HVGO, 300 °C, 325 °C and 350 °C and shows a decrease upon heating to 400 °C. The inset in Figure 3 shows the N\textsubscript{1}O\textsubscript{2}, S\textsubscript{1}O\textsubscript{4} and O\textsubscript{4} class analyses in more detail. The relative abundances of these classes all decrease with an increase in treatment temperature. However, the low relative abundance of these classes suggests they are not responsible for the large decrease in TAN upon thermal treatment.

Isobundance contours for plots of DBE versus the carbon number for the O\textsubscript{2} class are shown in Figure 5.4.

![Figure 5.4](image)

**Figure 5.4:** Color-coded isoabundance contours for plots of double bond equivalents (DBE) versus the carbon number for the O\textsubscript{2} class derived from negative-ion ESI FT-ICR MS in heavy vacuum gas oil (top left), 300 °C liquid product (top center), 325 °C liquid product (top right), 350 °C liquid product (bottom left), and 400 °C liquid product (bottom right).

Species with DBE=3 (non-aromatic, consistent with a general formula of R(CH\textsubscript{2})\textsubscript{2}n=COOH, where R is predicted to be two cyclopentane or cyclohexane rings\textsuperscript{105} have the highest relative abundance in all samples.
and DBE values range from 1-16, with little change in the carbon number distribution. The O₂ speciation of the liquid products shows little alteration during thermal treatment. Thus, the O₂ class composition for the liquid products appears to have little effect on the TAN.

**Figure 5.5** shows isoabundance contours for plots of DBE versus the carbon number for the S₁O₂ class.

Figure 5.5: Color-coded isoabundance contours for plots of double bond equivalents (DBE) versus the carbon number for the S₁O₂ class derived from negative-ion ESI FT-ICR MS in heavy vacuum gas oil (top left), 300 °C liquid product (top center), 325 °C liquid product (top right), 350 °C liquid product (bottom left), and 400 °C liquid product (bottom right).

The carbon number and DBE distributions are similar for the HVGO feed and the liquid products up to the 400 °C treatment temperature, where there is a slight increase in carbon number and DBE. The bimodal distribution, 4-5 DBE and 7-8 DBE, both centered near a carbon number
of 30, suggest two stable core structures. Proposed structures of a thiophene core and a benzothiophene core plus a carboxylic acid are consistent with DBE values of 4 and 7. The HVGO, with highest TAN, shows higher abundance of the lower DBE core structure. Upon thermal treatment the more aromatic core structure is favored. The N$_1$O$_2$, S$_1$O$_4$ and O$_4$ species show similar species in all four samples (data not shown). In general, the carbon number range narrows upon increased treatment temperature.

The inert sweep gas from the thermal reactor for the 350 °C and 400 °C treatment temperatures was condensed and analyzed. The TAN values of the condenser products are high (see Table 5.1) and suggest a large amount of naphthenic acids.

### Table 5.1: Thermal Reactor Liquid and Condenser Products Negative-Ion ESI FT-ICR MS Class Analysis

<table>
<thead>
<tr>
<th>Class</th>
<th>Relative Abundance (% total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_1$O$_2$</td>
<td></td>
</tr>
<tr>
<td>S$_1$O$_2$</td>
<td></td>
</tr>
<tr>
<td>S$_2$O$_2$</td>
<td></td>
</tr>
<tr>
<td>S$_1$O$_3$</td>
<td></td>
</tr>
<tr>
<td>S$_1$O$_4$</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td></td>
</tr>
<tr>
<td>O$_3$</td>
<td></td>
</tr>
<tr>
<td>O$_4$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.6: Heteroatom class distribution (heteroatom content) for Athabasca bitumen HVGO thermal treatment liquid products and the corresponding condenser products for the 350 °C and 400 °C treatment temperatures derived from negative-ion ESI FT-ICR mass spectra.
The heteroatom content of the light end products at the 350 °C and 400 °C treatment temperatures are found in Figure 5.6 along with the corresponding liquid products at the same treatment temperature. The condenser products are dominated by the O₂ class and contain a small amount of S₁O₂ species and the 400 °C condenser product contains more multi-heteroatom species (S₁O₃, O₃, O₄) than the 350 °C condenser product. The high abundance of acids found in the condensed sweep gas may account for the decrease in TAN of the liquid products with increase in treatment temperature.

Figure 5.7 shows isoabundance contours for plots of DBE versus the carbon number for the O₂ class of the condensed inert sweep gas from the 350 °C and 400 °C treatment temperatures and their corresponding liquid products at the same treatment temperature. The 350 °C condenser product contains species up to DBE 9, whereas the 400 °C species extends to DBE 13. Species with DBE=3 are still prominent, however the carbon number shifts from 33 in the HVGOs to ~22 for the condenser products, suggestive of lower boiling acid species.

Similarly, Figure 5.8 shows color-coded plots of double bond equivalents versus carbon number for the S₁O₂ class. Again the 400 °C product extends to higher DBE (12) than the 350 °C sample (DBE 8). The condenser products favor the less aromatic core structure (4-5 DBE). These low carbon number species observed in the condensed sweep gas are boiling off at the higher treatment temperatures and are carried into the condenser by the inert sweep gas. The loss of these species appears to contribute more to the decrease in TAN than broader compositional changes in acid speciation.
Figure 5.7: Isoabundance contours for plots of double bond equivalents (DBE) versus the carbon number for the O₂ class derived from negative-ion ESI FT-ICR MS in the 350 °C condenser product (top left), 350 °C liquid product (top right), 400 °C condenser product (bottom left), and 400 °C liquid product (bottom right).
Figure 5.8: Isoabundance contours for plots of double bond equivalents (DBE) versus the carbon number for the $S_1O_2$ class derived from negative-ion ESI FT-ICR MS in the 350 °C condenser product (top left), 350 °C liquid product (top right), 400 °C condenser product (bottom left), and 400 °C liquid product (bottom right).
Conclusions

Ultra-high resolution FT-ICR MS is well suited to study the compositional changes of thermally treated petroleum samples. The TAN decreases with increasing thermal treatment temperature; however ESI FT-ICR MS reveals no change in the naphthenic acid (O\textsubscript{2} class) composition of the liquid products. A shift to higher aromatic core structure is observed for the S\textsubscript{1}O\textsubscript{2} class at higher treatment temperature. Changes in relative abundance for multi-heteroatom containing classes such as N\textsubscript{1}O\textsubscript{2}, S\textsubscript{1}O\textsubscript{4} and O\textsubscript{4} are not likely to account for the large decrease in TAN with increased treatment temperature. ESI FT-ICR MS identifies a high relative abundance low carbon number O\textsubscript{2} species in the high TAN condensed sweep gas products. These low carbon number species are likely boiling off at higher treatment temperatures. The loss of these species likely contributes to the reduction in TAN more than any molecular transformations.
CHAPTER 6.

SELF-ASSOCIATION OF ORGANIC ACIDS IN PETROLEUM AND CANADIAN BITUMEN CHARACTERIZED BY LOW-RESOLUTION AND HIGH-RESOLUTION MASS SPECTROMETRY


Summary

We examine solution-phase aggregation for a whole crude oil, whole bitumen, and bitumen distillate fractions by negative-ion electrospray ionization [negative-ion ESI] detected by both high-resolution [Fourier transform ion cyclotron resonance (FT-ICR)] and low-resolution [linear quadrupole ion trap (LTQ)] mass spectrometry (MS). Aggregate formation for both crude oil and bitumens is concentration-dependent. At high concentrations (i.e., >1 mg/mL), the disruption of noncovalent interactions between heteromultimers by low-energy collision-activated dissociation (CAD) yields LTQ dissociation mass spectra with molecular-weight distributions identical to those observed by FT-ICR MS analysis at lower concentrations for purely monomeric species. These materials can exist as aggregates in solution even at high dilution (less than 0.1 mg/mL). We demonstrate the concentration and boiling point dependence for multimerization of polar acidic species in the Athabasca bitumen and bitumen distillates. Interestingly, the lowest boiling distillation cut (375-400 °C) displays the highest aggregation tendency, with dimers at concentrations as low as 0.05 mg/mL. Higher boiling point distillation cuts display a decreased aggregation tendency with an increasing cut point. High-resolution negative-ESI FT-ICR MS of the bitumen distillation fractions reveals the elemental composition, and thus the class, type, and carbon number of the multimeric species.
Acidic heteroatomic classes for the distillation cut multimers include O₄, S₁O₄, O₃, S₁O₃, N₁O₂, and N₁S₁O₂. The most abundant multimers for the 375-400 °C distillation cut are O₄ species, whereas the 450-475 °C cut contains N₁O₂ multimers in the highest relative abundance. Changes in multimer heteroatom content as a function of the monomer composition and distillation cut suggest that aggregation depends upon the chemical functionalities of the monomer species.

**Introduction**

The molecular weight distribution (MWD) of petroleum and petroleum derived materials is widely debated. Simply, the MWD’s determined by various techniques (e.g. size exclusion chromatography (SEC), vapor pressure osmometry (VPO), fluorescence depolarization and mass spectrometry) differ significantly. Many experiments report low molecular weight (100-2000 Da) but a few suggest much higher molecular weight (100-50,000 Da or higher). It is known that the tendency for petroleum molecules (including but not limited to asphaltenes) to self-associate complicates the determination of true monomeric MWDs. As a result, analytical techniques that require high concentration (VPO) or that use solvents that may promote aggregation (gel permeation chromatography (GPC) and SEC) can yield molecular weight distributions that reflect aggregate molecular weight and not that of the true monomer.

Mass spectrometry with various ionization methods has been used extensively to examine the MWD of petroleum. Boduszynski used field ionization/field desorption ionization (FI/FD) to conclude that the upper limit of the molecular weight distribution of petroleum is approximately 2,000 Da. Del Rio and Philp found similar distributions (< 2,000 Da) for a waxy yellow crude and a solid bitumen by FI MS. Plasma desorption
(PD) mass spectrometry based on Californium-252 shows distributions extending to ~2,500 Da,\(^{140, 141}\) all supporting a low MWD for petroleum; however, PD MS can yield multimeric species.\(^{155, 156}\) Laser desorption (LD) and matrix-assisted laser desorption ionization (MALDI) mass spectrometry have been used extensively to characterize the MWD for petroleum and petroleum asphaltenes with mixed results.\(^{128-131, 133, 137, 139, 142}\) However, Tanaka and Winans recently addressed the difficulties in obtaining reproducible and accurate molecular weight distributions from LD/MALDI MS.\(^{142}\) Problems include formation of multimer ions, fragmentation, selective ionization, insufficient desorption, and laser power dependence. Mass spectrometric ionization methods, such as electrospray ionization (ESI), field desorption, and atmospheric pressure photoionization routinely display MWD’s for petroleum and asphaltenes from 300-1500 Da, but always below 4,000 Da.\(^{28, 39, 43, 74, 75, 157, 158}\)

Aggregation of petroleum asphaltenes is well documented.\(^{139, 143-153}\) However, the reported onset of aggregation varies substantially. Recently, it has been suggested that asphaltenes aggregate at much lower concentrations (~ 0.05-150 mg/mL) than previously reported and may aggregate in step-wise fashion rather than micelle-like aggregation.\(^{150}\) Asphaltene molecules have been proposed to aggregate through π-π stacking.\(^{149, 159}\) However, it has been suggested that more complex association mechanisms may be at work, including hydrogen-bonding contributions.\(^{139, 160}\)

We have previously reported the observation of multimer species of polar components in diesel fuel\(^{95}\) and petroporphyrins.\(^{161}\) However, at sufficiently low concentration (< 0.1 mg/mL of total sample, so that the concentration of any individual molecular component is less than 1 µM), aggregation of polar components is typically not observed. Here, we report low-resolution linear quadrupole ion trap mass spectrometry (LTQ, Thermo Electron Corp., San Jose, CA) and high-resolution FT-ICR mass spectra that unequivocally establish the aggregation tendency and
monomer and multimer distributions for acidic species in a whole crude oil, Athabasca bitumen, and its associated distillation cuts. The tandem MS (MS\textsuperscript{n}) capability, high ion capacity, and high upper mass limit (4 kDa) of the LTQ mass spectrometer make it well suited to examine aggregation in petroleum samples. Suspected multimers may be rapidly isolated and dissociated at various dissociation energies to generate either monomer molecular weight distributions (low-energy dissociation) or fragmentation spectra (high-energy dissociation). The systematic evaluation of the multimerization/dissociation/fragmentation tendencies of standards sets the energy threshold between multimer dissociation and the onset of fragmentation. The ultrahigh mass resolving power (m/Δm\textsubscript{50%} > 350,000, in which Δm\textsubscript{50%} is the mass spectral peak full width at half-maximum peak height) and high mass accuracy (better than 500 ppb) of FT-ICR MS allow the assignment of a unique elemental composition to each peak in the mass spectrum.\textsuperscript{3-5} Thus, elemental composition assignment allows organization of compounds by class (heteroatom content), type (double bond equivalents, the number of rings and/or double bonds (DBE)), and carbon number. Therefore, the FT-ICR MS results identify polar chemical functionality preference in the formation of multimeric species. We present the concentration dependence for multimer formation as well as compositional information on monomer and dimer distributions of self-associated acids in petroleum derived samples.

**Experimental Methods**

**Sample Description and Sample Preparation for ESI MS**

Model compounds were obtained from Sigma-Aldrich (St. Louis, MO). Crude oil samples were supplied by Baker Petrolite (Sugar Land, TX). Athabasca bitumen and bitumen distillation cuts (375-400 °C, 450-
475 °C and 500-525 °C) were obtained from The National Centre for Upgrading Technology (Devon, AB, Canada).

Saturated solutions of model compounds were prepared in 50:50 (v/v) toluene:methanol with 0.1% ammonium hydroxide (~65 fM). Bitumen and crude oil samples were diluted to 1 mg/mL in a 50:50 (v/v) toluene:methanol mixture and used without additional purification.

Distillation cuts for 375-400 °C, 450-475 °C and 500-525 °C were prepared at concentrations of 0.01, 0.05, 0.1, 0.5, 1.0, 5.0 and 10 mg/mL in a 50:50 (v/v) toluene:methanol mixture. Ammonium hydroxide was added (10 µL NH₄OH/1 mL sample, ~65 fM) to ensure efficient deprotonation for negative-ion electrospray analysis. All solvents were HPLC grade obtained from Fisher Scientific (Pittsburgh, PA).

**Instrumentation**

All FT-ICR MS experiments were performed on the 9.4 T ESI FT-ICR mass spectrometer described in Chapter 1. Negative-ion electrospray mass spectra (broadband and collision-activated dissociation (CAD) MSⁿ) were acquired with a linear quadrupole ion trap mass spectrometer (LTQ, Thermo Electron Corp., San Jose, CA). Optimum collision energy for CAD fragmentation varies linearly with m/z. Therefore, in the LTQ mass spectrometer the collision energy is normalized for each m/z value selected for dissociation (Normalized Collision Energy™, NCE).¹⁶²,¹⁶³ Electrospray conditions for LTQ analysis were analogous to those described above.

**Mass Calibration and Data Analysis**

FT-ICR mass spectra were internally calibrated with respect to a homologous series of ions each containing two oxygen atoms, present in high abundance in each sample.⁷⁴ Singly-charged ions (250 < m/z <
with relative abundance greater than six times the standard deviation of baseline noise were exported to a spreadsheet. Measured masses were converted from the IUPAC mass scale to the Kendrick mass scale\textsuperscript{19} for identification of homologous series. Kendrick mass defect analysis was used for peak assignments as previously described.\textsuperscript{20}

**Results and Discussion**

\textbf{MS}^n evidence that high-mass species consist of non-covalent aggregates

Molecular weight ranges between 300-1000 Da are commonly encountered in the ESI FT-ICR MS analysis of petroleum samples. However, due to known mass discrimination in ion transmission from the ion accumulation device to the ICR cell (due to different time of flight for ions of different mass), we routinely verify molecular weight distributions obtained by FT-ICR MS with a low-resolution linear quadrupole trap mass spectrometer. In most cases, the low-resolution and high-resolution mass spectra display near-identical MWD’s for petroleum. However, we recently observed anomalous behavior for an African crude oil. \textbf{Figure 6.1a} shows a low-resolution negative-ion ESI linear quadrupole trap mass spectrum of the African crude oil. We had not previously encountered such a wide MWD (up to m/z 2,000) with our low-resolution instrument and the higher-mass species are not seen by ESI FT-ICR MS (Fig. 6.1e). We therefore suspected multimer formation and undertook collisionally activated dissociation (CAD) \textbf{MS}^n experiments.

\textbf{Figure 6.1b} shows an \textbf{MS}^2 product ion spectrum from precursors of m/z 2,000 ± 50 isolated from the broadband ion population and subjected to low-energy CAD at 20% normalized collision energy (NCE). The product ions range from 1,000 < m/z < 1,800, centered at m/z 1,500. Similarly, \textbf{MS}^3 CAD (20% NCE) of the m/z 1,500 ± 50 products of
the MS² experiment of Figure 6.1b gave the products shown in Figure 6.1c, to yield ions of 500 < m/z < 1,300, centered at m/z 800. Figure 6.1d shows the MS⁴ spectrum produced by isolation and 20% NCE of ions of m/z 1000 ± 50 from the experiment of Figure 6.1c, and subjected to low-energy (20% NCE) CAD. Further isolation/dissociation (MS⁵) resulted in no change to the molecular weight distribution. Signal-to-noise ratio decreases at each stage of MS/MS, because ions of a limited m/z range dissociate to give a broader m/z distribution each time.

The low collision energy in Figs. 6.1b-6.1d ensures that covalent bonds are not broken, hence, the successive reduction in molecular weight after each stage of MS/MS in Figs. 6.1a-6.1d indicates that the species higher in mass than ~800 Da represent non-covalent adducts (dimers, trimers, tetramers). (High-resolution FT-ICR MS (see below) confirms that the ions are singly-charged, based on the separation by m/z = 1 between species of the same chemical formula containing $^{13}\text{C}^{12}\text{C}_{\text{c-1}}$ and $^{12}\text{C}_{\text{c}}$.) Moreover, the multimers are hetero- rather than homo-adducts, because a narrow isolated mass distribution of precursor ions leads to a broad distribution of product ion masses.

Figure 6.1e shows a high-resolution negative-ion ESI FT-ICR mass spectrum for the same African crude oil. The monomer distribution from low-resolution MS4 of the broadband mass spectrum (Figure 6.1d) is essentially the same as the high-resolution mass spectrum (Figure 6.1e). Ergo, multimers presumably dissociate due to numerous collisions with neutral atmospheric gas in the octopole ion trap during prolonged ion accumulation prior to subsequent ESI FT-ICR MS detection. Heteroatom class, type (rings plus double bonds) and carbon number analysis of the FT-ICR MS data reveal that the African oil contains an unusually high relative abundance of the O₂ class (85% of the total ion current). Other identified heteroatom classes include N₁, O₁, N₁O₂, N₁O₁, O₃ and O₄ in order of decreasing relative abundance. The high abundances of Oₓ and
Figure 6.1: Low-resolution negative-ion ESI LTQ mass spectra (a-d) and high-resolution negative-ion ESI FT-ICR mass spectrum (e) of an African crude oil: (a) broadband (1mg/mL); (b) MS/MS for precursor ions of m/z 2,000 ± 50, 20% normalized collision energy (NCE); (c) MS3 for MS2 product ions of m/z 1,500 ± 50, 20% NCE; (d) MS4 for MS3 product ions of m/z 1,000 ± 50, 20% NCE; (e) FT-ICR MS broadband mass spectrum of the same crude oil (1 mg/mL).
N\textsubscript{1}O\textsubscript{x} classes may explain the anomalous high-mass aggregates observed by low-resolution LTQ mass spectrometry of this material.

**Aggregation for model compounds**

The MS\textsuperscript{n} confirmation of acidic multimeric species in the low-resolution analysis of the African crude oil combined with the high relative abundance of O\textsubscript{x} and NO\textsubscript{x} classes determined by FT-ICR MS led us to select a set of model compounds to characterize negative-ion multimer formation by low-resolution mass spectrometry. Because negative-ion ESI preferentially ionizes species with a labile proton, we chose model compounds with easily deprotonated acidic functional groups (e.g., pyrollic nitrogen, phenolic and carboxylic acid containing species). The broadband low-resolution mass spectrum of the model compound, 1,1'-binaphthalene-8,8'-dicarboxylic acid (**Figure 6.2**, top) reveals a trimer at m/z 1,026 and dimer at m/z 684. Low-energy (12% NCD) CAD of the dimer yields the monomer (Fig. 6.2, middle). Similar isolation of the trimer and even lower-energy (9% NCE) CAD yields the dimer and the monomer (Fig. 6.2, bottom). The absence of monomer fragment ions in the CAD product ion mass spectra ensures that the CAD energy is sufficiently low to disrupt only non-covalent interactions, without inducing fragmentation. (The gas-phase reaction minor product of m/z 510 appears only on isolation of the trimer.)

**Figure 6.3** shows the dissociation profiles for CAD of the dimer ion for each of nine model compounds, based on the peak height ratio (dimer/monomer) as a function of normalized collision energy. The onset of monomer fragmentation is listed in **Table 6.1** for each model compound (expressed as normalized collision energy). Both of the highly aromatic carbazoles, 7H-dibenzo[c,g]carbazole and 5,11-dihydro-6H-benzo(A)carbazole, dissociate at very low energy (3-4% NCE for 50% dissociation) 2,2'-biquinoline]-4,4'-dicarboxylic acid, 1,1'-binaphthalene-
8,8'-dicarboxylic acid, and 1-pyrenol form successively stronger dimers, but those dimers dissociate more abruptly (over a more narrow NCE range) than do the carbazoles: 1,1':2',1''-terphenyl]-3',5'-dicarboxylic acid was the most stable toward dissociation. Saturated fatty acids (eicosanoic acid, tetracosanoic acid, and octacosanoic acid) dissociate abruptly at NCE values similar to those for the previous three model compounds. Additional carboxylic acid groups appear to favor dimer formation, presumably driven by the formation of hydrogen bonds and/or proton-bound dimers. However, incorporation of nitrogen into the aromatic ring system in [2,2'-biquinoline]-4,4'-dicarboxylic acid results in a weaker dimer (lower dissociation threshold) than the two other dicarboxylic acid-containing model compounds. These dissociation
energy profiles show how dimer stability depends on heteroatom content and aromaticity of the monomers.

Table 6.1: Model compound structure and monomer fragmentation energy.

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Monomer Structure</th>
<th>Monomer Fragmentation Energy (NCE (% of maximum))</th>
</tr>
</thead>
<tbody>
<tr>
<td>7H-dibenzo[c,g]carbazole</td>
<td>![Image]</td>
<td>45</td>
</tr>
<tr>
<td>5,11-dihydro-6H-benzo(A)carbazole</td>
<td>![Image]</td>
<td>45</td>
</tr>
<tr>
<td>[2,2’-biquinoline]-4,4’-dicarboxylic acid</td>
<td>![Image]</td>
<td>~ 20 (CO loss)</td>
</tr>
<tr>
<td>1,1’-binaphthalene-8,8’-dicarboxylic acid</td>
<td>![Image]</td>
<td>18 (CO loss)</td>
</tr>
<tr>
<td>1-pyrenol</td>
<td>![Image]</td>
<td>60</td>
</tr>
<tr>
<td>[1,1’:2’,1”-terphenyl]-3’,5’-dicarboxylic acid</td>
<td>![Image]</td>
<td>~20 (CO loss)</td>
</tr>
<tr>
<td>Eicosanoic acid</td>
<td>![Image]</td>
<td>27</td>
</tr>
<tr>
<td>Tetracosanoic acid</td>
<td>![Image]</td>
<td>35</td>
</tr>
<tr>
<td>Octacosanoic acid</td>
<td>![Image]</td>
<td>28</td>
</tr>
</tbody>
</table>
Figure 6.3: Peak height ratio (dimer/monomer) versus normalized collision energy for negative-ion ESI LTQ MS/MS of each of six model compounds. (Compound names are listed in Table 6.1.)

**Effect of concentration on multimer formation**

We have previously determined heteroatom class, type, and carbon number variation for a set of Athabasca bitumen distillation cuts: aromaticity and carbon number increase with increasing boiling point with slight changes in chemical classes.\(^\text{114}\) To assess whether or not these class and/or type changes as a function of distillation cut play a role in self-association, we analyzed three distillation cuts (375-400 °C, 450-475 °C and 500-525 °C) by electrospray ionization low-resolution linear quadrupole mass spectrometry (Figure 6.4) and high-resolution FT-ICR mass spectrometry (Figure 6.5), at concentrations from 0.01 mg/mL to 10 mg/mL.
Figure 6.4: Low-resolution negative-ion ESI LTQ mass spectra of three Athabasca bitumen distillation cuts at 0.05, 0.1, 0.5, and 1.0 mg/mL. Top: 375 – 400 °C; Middle: 450 – 475 °C; Bottom: 500 – 525 °C.

The lowest boiling cut, 375-400 °C (Fig. 6.4, top) clearly aggregates at concentrations as low as 0.05 mg/mL and the dimers are already more abundant than the monomers at 0.1 mg/mL. Moreover, trimers begin to appear at 1 mg/mL as a small hump around m/z ≈ 950. Aggregation is present, but less pronounced, for the 450-475 °C distillate cut (Fig. 6.4,
middle) and even less pronounced for the 500-525 °C cut (Fig. 6.4, bottom). Thus, as boiling point increases the aggregation tendency actually decreases. Prior FT-ICR MS experiments showed higher aromaticity (DBE) and carbon number with increasing boiling point. We therefore conclude that higher aromatic species and/or those with higher carbon number (higher degree of alkylation) are less likely to self-associate than lower-aromaticity or even non-aromatic polar acidic species. Unfortunately, the resolution and mass accuracy of the LTQ mass spectrometer preclude direct identification of the species responsible for multimer formation. We therefore proceed to high-resolution ESI FT-ICR MS, for determination of heteroatom class, type and carbon number distribution for monomers and multimers.

Negative-ion ESI FT-ICR broadband mass spectra show aggregation similar to that in low-resolution LTQ mass spectra: the lowest boiling cut species aggregate to a greater extent and at lower concentration than do the higher boiling components (data not shown). However, FT-ICR MS required higher concentration for aggregation (see Fig. 6.5 for the 375-400 °C distillation cut). In FT-ICR MS, ions are externally accumulated (0.1-30 s duration) at high pressure (3.5 mTorr). Collisions with neutral atmospheric gas (O₂ and N₂) in the octopole ion trap dissociate non-covalent aggregates. Thus, higher sample concentration must be used to observe multimer formation. At 1 mg/mL (Fig. 6.5, top), a typical sample concentration for ESI FT-ICR mass analysis, aggregation is clearly evident. As the concentration increases to 5 mg/mL (Fig. 6.5, middle) and 10 mg/mL (Fig. 6.5, bottom) the multimers increase in abundance relative to monomers.
Heteroatom class, type, and carbon number characterization of multimers

FT-ICR MS analysis allows determination of class, type and carbon number for both the monomer and multimeric species and thus affords chemical insight into which species preferentially form multimers. Bitumen and bitumen distillation cut monomer distributions both exhibit O$_2$ (presumably naphthenic acids) and S$_1$O$_2$ classes in high abundance.$^{114,164}$ Figure 6.6 shows the class analysis for the 375 – 400 °C distillation cut at 1, 5 and 10 mg/mL. The monomer distribution extends up to m/z ≈ 500 (see Fig. 6.5); for each class, monomers and multimers could be distinguished according to the DBE values for the lowest- and highest-mass members of homologous series. Figure 6.6
shows that O₄ multimers increase (whereas O₂ monomers decrease) in relative abundance with increasing bitumen concentration, suggesting that O₄ multimers form at the expense of O₂ monomers. Similarly, the S₁O₄ class relative abundance increases with concentration, most likely due to aggregation of O₂ and S₁O₂ monomers.

Figure 6.6: Heteroatom class distribution (heteroatom content) for Athabasca Bitumen 375-400 °C distillation cut at 1, 5 and 10 mg/mL, derived from the high-resolution ESI FT-ICR mass spectra of Fig. 6.5.

Figure 6.7 shows isoabundance color-coded plots of double bond equivalents versus carbon number for O₂ monomers (Fig. 6.7, left) and O₄ multimers (Fig. 6.7, right) for the 375-400 °C distillation cut at 1 mg/mL. The monomer distribution reaches a maximum in abundance at 3 DBE, suggesting non-aromatic carboxylic acids, with a range of 1 to 9 DBE. Carbon numbers range from 17 to 36 with highest abundance at ~24. The O₄ multimers exhibit higher DBE (3-13, with maximum at 6) and carbon number (33-52, with maximum ~42). The odd number of
hydrogen atoms in the multimers suggests proton-bound dimers and/or hydrogen bonded dimers. Either way, the multimer has a calculated DBE value lower by one unit than the summed DBE values for the individual monomers.

![Graph](image)

Figure 6.7: Color-coded isoabundance contours for plots of double bond equivalents (DBE) vs. carbon number for the O_2 monomer (left) and O_4 dimer (right) classes for the 375-400 °C Athabasca bitumen distillation cut at 1 mg/mL concentration.

Although the DBE value doubles (from average of 3 to 6) on formation of multimers from monomers, the carbon numbers do not (from average of 24 to 40), presumably due to discrimination against low-mass ions by the ion accumulation and transmission multipoles for the broadband FT-ICR mass spectra: compare the relative abundances of the monomer and multimer distributions for the LTQ (Fig. 4 (top) and FT-ICR (Fig. 5), both at 1 mg/mL.) Aggregates for the 500 – 525 °C cut were not observed by FT-ICR MS, suggesting weak aggregation.
**Figure 6.8** shows class distributions for the 375-400 °C and 450-475 °C cuts.

**Athabasca Bitumen Class Analysis**  
375 – 400 °C and 450 – 475 °C Cuts  
Negative-Ion ESI FT-ICR MS

![Graph showing class distributions](image)

Figure 6.8: Heteroatom class distribution for 375-400 °C and 450-475 °C Athabasca bitumen distillation cuts at 5 mg/mL.

O$_2$ monomers increase and O$_4$ multimers decrease in relative abundance with increased boiling point. Increased cut point yields an increase in carbon number for all species and an increase in DBE, but with high relative abundance hot spots at the same DBE values.\textsuperscript{114} In addition, saturated fatty-acids readily form multimers at low concentration by LTQ and FT-ICR MS (data not shown). The decrease in O$_4$ multimers with increasing cut point suggests that increase in carbon number (alkylation) of O$_2$ monomers affects multimerization. Experiments to investigate that effect are difficult due to the lack of high DBE, highly alkylated O$_2$ model compounds. The decrease in O$_4$ multimers results in a relative increase in abundance for multi-functional nitrogen-containing multimers such as N$_1$O$_2$ and N$_1$S$_1$O$_2$. The nature of the nitrogen (i.e., pyrollic or
pyridinic) involved in multimerization is unknown; however future MS\textsuperscript{n} experiments are aimed to address this issue. The low relative abundance of sulfur-containing components makes the determination of their contribution to multimerization difficult.

The extent of aggregation of O\textsubscript{2} monomers decreases with increase in boiling point (Figure 6.9).

![Figure 6.9: Color-coded isoabundance contours for plots of DBE vs. carbon number for O\textsubscript{4} aggregates from 375-400 °C (left) and 450-475 °C (right) Athabasca bitumen distillation cuts at 5 mg/mL concentration.](image)

Although the abundance of all O\textsubscript{4} multimers drops in proceeding from 375-400 °C to 450-475 °C, the O\textsubscript{4} DBE range is similar but with an increase in carbon number range. Low DBE O\textsubscript{4} multimers are present at higher boiling point, despite an increase in DBE for the O\textsubscript{2} monomers. The depletion of low carbon number, low DBE O\textsubscript{2} species known to
readily aggregate may explain the decrease in O₄ multimers at higher cut point.

Isoabundance color-coded contours for a plot of DBE vs. carbon number for N₁O₂ multimer class at 5 mg/mL are shown in Figure 6.10 for the 375-400 °C (Fig. 10, left) and 450-475 °C (Fig. 10, right) distillation cuts.

![Figure 6.10](image)

Figure 6.10: Color-coded isoabundance contours for plots of DBE vs. carbon number for N₁O₂ aggregates from 375-400 °C (left) and 450-475 °C (right) Athabasca bitumen distillation cuts at 5 mg/mL concentration.

For the 375-400 °C cut, DBE ranges from 9-18, with a maximum at 11-12. Carbon numbers center at 42 and range from 30 to 51. One possibility for a calculated DBE of 9 for a neutral N₁O₂ molecule (DBE 10) is a saturated carboxylic acid (1 DBE) associated with a 9 DBE nitrogen-containing molecule (either pyridinic or pyrrolic nitrogen). The 450-475 °C N₁O₂ aggregates show a shift to higher DBE and carbon
number: DBE peak at 14 and range from 9-23. Carbon numbers range from 40 to 65 with an average of 52. The increase in 3 DBE from 11 in the 375-400 °C cut to 14 in the 450-475 °C cut is consistent with the addition of a benzene ring to the aromatic core. The increase in DBE and relative abundance for the N$_1$O$_2$ multimers of the 450-475 °C cut indicates that aromaticity plays a more important role in association for more aromatic, nitrogen species than for non-aromatic carboxylic acid species.

Future research will aim to identify those monomers that form stable multimers. Tandem mass spectrometry of individually isolated multimers should identify the class, type and carbon number of each monomer that contributes to a multimer. NCE dissociation energy profiles of gas-phase multimers with known dissociation energies will be constructed to determine the association energy of the petroleum multimers. In addition, the multimerization tendency of basic species in crude oil will be evaluated by positive-ion ESI LTQ and FT-ICR MS combined with tandem mass spectrometry to determine the nature of nitrogen-containing species involved in multimerization.

**Conclusions**

The aggregation of bitumen acidic species was not initially observed by ESI FT-ICR MS due to the low concentration (≈ 1 mg/mL) used in those experiments. In addition, lengthy external ion accumulation in the presence of neutral gas facilitates dissociation of weakly bound aggregates. Our results suggest that methods for molecular weight determination that require high concentration (VPO) or solvents that promote aggregation (SEC) can be skewed toward high molecular weight due to aggregate formation. In addition, MS methods that do not disrupt non-covalent aggregates yield erroneous high molecular weight distributions.
Anomalous behavior (a broad molecular weight distribution extending up to 2 kDa) is observed for an African crude oil at 1 mg/mL by low resolution negative-ion ESI MS. Negative-ion FT-ICR MS of the same crude oil shows a different molecular weight distribution and an abnormally high relative abundance of Oₓ and N₁Oₓ classes. Subsequent low-resolution MS experiments confirm multimer formation and regenerate the monomer molecular weight distribution observed by FT-ICR MS. Tandem mass spectrometry of acidic standards yields no fragmentation of monomer species and establishes aggregation and dissociation dependence on class and aromaticity.

Low-resolution MS of a 375-400 °C Athabasca bitumen distillation cut displays aggregation at concentrations as low as 0.05 mg/mL, in agreement with high-Q ultrasonic measurements for asphaltene aggregation. However, FT-ICR MS data reveal that non-aromatic (DBE < 4) O₂ species are responsible for the bulk of multimer formation (O₄ multimers). Thus, polar interactions can replace π-π interactions of aromatic cores in aggregation at low concentration. Higher-boiling bitumen distillation cuts exhibit lower tendency for aggregation (by both low and high resolution MS) and show a decrease in O₄ multimers and relative increase in more aromatic N₁O₂ multimers.

FT-ICR MS analysis of bitumen distillation cuts reveals the same aggregation trends as low resolution MS: namely, increase in cut point yields less aggregation. Class, type and carbon number analysis show that non-aromatic O₂ monomer species are consumed to form O₄ aggregates. The loss of those non-aromatic (lower boiling) O₂ species with increased cut point may help explain the decrease in O₄ multimer formation at higher distillation temperature. In addition, the type (DBE) of O₄ aggregates does not change with increasing cut point, again suggesting that polar interactions can account for aggregation. Type analysis of N₁O₂ aggregates do show an increase in DBE with increase in
bitumen cut point, supporting the idea that aromaticity plays a more important role in aggregation for higher boiling distillates.
CHAPTER 7.

ASPHALTENE INHIBITOR SPECIFICITY RELATED TO DETAILED POLAR CHEMICAL COMPOSITION DERIVED FROM FT-ICR MASS SPECTROMETRY

Summary

We examine oil-specific asphaltene inhibitor chemistry of two chemically distinct asphaltene inhibitors. Laboratory and field tests show oil specific asphaltene inhibitor performance for two geographically distinct crude oils. The crude oils and asphaltenes were characterized by a variety of analytical techniques which include total acid number (TAN), elemental analysis, Fourier transform infrared spectroscopy (FT-IR) and Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS). ESI FT-ICR MS reveals differences in the relative abundance of heteroatom-containing compound classes in the two crude oils and the two asphaltenes. We identify acidic and/or basic species that may be responsible for the observed differences in inhibitor chemistry. Asphaltene inhibitor specificity can be explained by acid-base type interactions between the inhibitor and polar species in the crude oils or asphaltene fractions. We present the first evidence of inhibitor effectiveness related to heteroatom content by detailed polar chemical composition derived from ESI FT-ICR MS.

Introduction

Problems Caused by Asphaltenes

Asphaltenes are the most aromatic and most polar component of crude oil and are typically defined by their solubility in benzene and insolubility in heptane or pentane. Asphaltenes are normally stable under reservoir conditions. However, as crude oil is produced, that stability may be disrupted by a number of factors; including pressure reductions, crude oil chemical composition changes, introduction of
miscible gases and liquids, addition of diluents and other oils, and oilfield operations such as acid stimulation and hot oiling. The deposition and precipitation of asphaltenes in an oil field can reduce the permeability of the reservoir, damage the formation and plug the wellbore and other tubing and oil field equipment.\textsuperscript{165-168}

**Asphaltene Inhibitors**

Chemical inhibitors are often added to the well to prevent asphaltene deposition. Due to proprietary secrets, the structure and chemistries of many commercial inhibitors are unknown. To this end, there are limited studies in the literature focused on commercial inhibitors. However, the use of amphiphiles for asphaltene inhibition has been studied\textsuperscript{169-175}, as well as ionic and non-ionic block copolymers.\textsuperscript{172, 176} Two important conclusions can be drawn from these studies; acid-base interactions contribute to asphaltene inhibition for ionic inhibitors and steric effects related to the size of the inhibitor (either aliphatic chain length or polymer chain length) are important to inhibitor effectiveness. However, few of these studies are structure based, but rather study the onset of asphaltene precipitation or the kinetics of asphaltene precipitation. Thus, here we analyze the detailed polar chemical composition of two geographically different crude oils and their precipitated asphaltenes by ESI FT-ICR MS to explore oil-specific asphaltene inhibition.

**FT-ICR MS for Petroleum Analysis**

FT-ICR MS is well suited for the analysis of complex petroleum\textsuperscript{4, 5, 18, 38, 43, 67, 74, 75, 95, 96, 123} and asphaltene\textsuperscript{177, 178} mixtures. The high mass resolving power of FT-ICR MS (\(m/\Delta m_{50\%} > 400,000\), in which \(\Delta m_{50\%}\) is the mass spectral peak full width at half-maximum peak height) allows closely spaced isobaric compounds, such as those with elemental
compositions differing by $^{12}\text{C}_3$ versus $\text{S}_1\text{H}_4$ (3.4 mDa), an important doublet in petroleum and asphaltene mass spectra which is unresolved in most other spectrometric techniques$^{3-5}$. Once the high number of spectral peaks are resolved, the high mass accuracy (better than 500 ppb) of FT-ICR MS allows the assignment of a unique elemental to each peak.$^3$ Thus, assigned elemental compositions allow compounds to be organized by class (heteroatom content), type (double bond equivalents, the number of rings and/or double bonds (DBE)), and carbon number. Therefore, FT-ICR MS identifies differences in asphaltene polar chemical functionality in relation to oil-specific asphaltene inhibitor specificity. We present compositional information on whole crude oil and precipitated asphaltenes of two geographically different crude oils related to the oil-specific inhibition of asphaltene precipitation by two chemically different asphaltene inhibitors.

**Experimental Methods**

**Sample and Inhibitor Description**

Two geographically distinct crude oils with oil-specific asphaltene inhibitor performance were analyzed. Oil A is an offshore Gulf of Mexico crude oil with 25° API gravity. Oil B is a land based European crude oil with an API gravity of 38°. Asphaltenes were precipitated with $n$-heptane by a modified IP143/57 procedure. Inhibitor A is polymer based with protic polar heads and aliphatic tails, inhibitor B is a non-polymeric amine based molecule with a polar head and an aliphatic tail.
Instrumentation

Asphaltene Inhibitor Selection Test

Centrifuge heptane precipitation tests were performed by the addition of chemical inhibitors to the crude oils at different treatment levels. 100 µL of treated crude oil was injected into 10 mL of heptane, shaken and allowed to stand for one hour after which it was centrifuged at 1,500 RMP for five minutes. The transmittance of the centrifuged solution was monitored with a Brinkmann 910 colorimeter at 570 nm (4 mm path length).

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectra were collected on a Mattson Galaxy FT-IR 5000 spectrometer. Samples were prepared to 65 mg/mL in chloroform and analyzed with in a solution potassium bromide cell (0.5 mm path length).

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

All electrospray FT-ICR MS experiments were performed on the 9.4 T ESI FT-ICR mass spectrometer described in Chapter 1. Crude oil samples were prepared at 1 mg/mL in a 50:50 (v/v) toluene/methanol mixture. Asphaltene samples were prepared at 1 mg/mL in a 60:40 (v/v) toluene/methanol mixture. Ammonium hydroxide (formic acid) was added at 1% (by volume, ~65 fM) to ensure efficient deprotonation (protonation) in negative (positive) ESI analysis. All solvents were HPLC-grade, obtained from Thermo Fisher Scientific (Pittsburg, Pa).
Mass Calibration and Data Analysis for FT-ICR MS

FT-ICR mass spectra were calibrated with respect to a homologous series of ions each containing two oxygen atoms (negative-ion ESI) or one nitrogen atom (positive-ion ESI), present in high relative abundance in each sample.\textsuperscript{74, 75} Singly charged ions (250 < m/z < 1,500) with a relative abundance greater than 6 times the standard deviation of the noise were exported to a spreadsheet. Measured masses were converted from the IUPAC mass scale to the Kendrick mass scale\textsuperscript{19} for identification of homologous series. Kendrick mass defect analysis was used for elemental composition assignment as previously described.\textsuperscript{20}

Results and Discussion

Oil-Specific Asphaltene Inhibitor Performance

Table 7.1 shows total acid number (TAN, mg KOH/1 g crude oil) and elemental analysis (C, H, N) for Oils A and B. As seen in Table 7.1, the bulk analyses do not indicate large differences in the crude oils. However, heptane precipitation results suggest different crude oil-inhibitor chemistry that is not clear from bulk analyses alone, as seen in Figure 7.1: The y-axis, asphaltene inhibitor relative effectiveness (%D), was determined using Equation 7.1, where T_S is the transmittance of the sample and T_B is the transmittance of the blank.

\[
%D = \left(1 - \left(\frac{\%T_S}{\%T_B}\right)\right) \times 100
\]  

(7.1)
Table 7.1: Total Acid Number and Elemental Analysis for the Crude Oils

<table>
<thead>
<tr>
<th></th>
<th>TAN (mg KOH/g oil)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil A</td>
<td>0.24</td>
<td>83.5</td>
<td>11.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Oil B</td>
<td>0.21</td>
<td>83.0</td>
<td>12.6</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Figure 7.1: Centrifuge heptane precipitation tests for both inhibitors effectiveness for both crude oils. Inhibitor A is specific to Oil A and inhibitor B is specific to Oil B. The y-axis is a relative measure of asphaltene inhibitor effectiveness.

Inhibitor A is specific to Oil A, whereas inhibitor B is specific to Oil B. Inhibitor A is polymer based with protic polar heads and aliphatic tails. Inhibitor B is a non-polymeric amine based molecule with a polar head and an aliphatic tail. The crude oils and their associated asphaltenes were analyzed to FT-IR spectroscopy to determine functional
group differences that may affect inhibitor chemistry. FT-IR spectra of the two crude oils were very similar (data not shown). However, the FT-IR spectra of the precipitated asphaltenes (Figure 7.2) shows a stronger absorbance at ~1700 cm\(^{-1}\) for Oil B, which is consistent with a carbonyl moiety. Due to the similarity of the bulk analyses and the FT-IR data, ESI FT-ICR mass spectrometry was used to identify acidic and/or basic species that may be responsible for different inhibitor specificity.

![Asphaltene FT-Infrared Spectrum](image)

Figure 7.2: FT-Infrared absorption spectra of the precipitated asphaltenes from Oil A and Oil B. Oil B asphaltenes have a stronger absorbance at ~1700 cm\(^{-1}\), consistent with a carbonyl moiety.

**Negative-Ion ESI FT-ICR MS of Whole Crude Oils**

The power of negative-ion ESI FT-ICR MS to characterize the acidic species in crude oils and asphaltenes has been shown.\(^{43, 74, 96, 177, 178}\) Common classes revealed in negative-ion ESI FT-ICR MS spectra include:
O₂ and S₁O₂, S₁O₃ and S₁O₄ (presumably carboxylic acid containing species, or naphthenic acids) and N₁, N₁S₁, N₁O₁ and N₁O₂ (neutral nitrogen, i.e. pyrrolic type nitrogen). The proton donating nature of the naphthenic acids may play an important role in asphaltene inhibitor chemistry, as discussed above.

**Figure 7.3** shows the class analysis (heteroatom content) for the whole crude oils derived from negative-ion ESI FT-ICR MS.

![Crude Oil Negative-Ion ESI FT-ICR MS: Class Analysis](image)

Figure 7.3: Heteroatom class distribution (heteroatom content) for selected classes from Oil A and Oil B, derived from high-resolution negative-ion ESI FT-ICR mass spectra. Oil A has a high relative abundance of O₂ species (naphthenic acids). The acid species may interact with basic inhibitor B before it is able to interact with asphaltenes. Oil B has higher relative abundance of neutral nitrogen (pyrrolic) containing species than Oil A.

The heteroatom distribution is remarkably different for crude oils A and B. Oil A has a high relative abundance of the O₂ class, likely composed of naphthenic acids. Oil A also contains S₁O₂ species, which are absent from the Oil B spectrum. Oil B contains more multi-heteroatom
containing classes than Oil A; most notably those with neutral nitrogen, $\text{N}_1$, $\text{N}_1\text{S}_1$, and $\text{N}_1\text{O}_1$.

Isoabundance color-coded contours for plots of DBE versus the carbon number for the $\text{O}_2$ class are shown in Figure 7.4. Both oils reach a maximum relative abundance at DBE=1, which suggest non-aromatic long chain carboxylic acids. The carbon number range for these species is similar for both oils, ~16-45. However, Oil A has the highest relative abundance species at C# 28-30, whereas those in Oil B are slightly lower at C# 25-26. In addition, Oil A has another area of high relative abundance at DBE=6 with carbon numbers of 24-28 and a higher relative abundance of species from DBE 2-13 than Oil B.

![Figure 7.4](image)

Figure 7.4: Color-coded isoabundance contours for plots of double bond equivalents (DBE) vs. carbon number for the $\text{O}_2$ class of Oil A and Oil B derived from the data shown in Fig. 7.3. Both oils contain high relative abundance of non-aromatic acids at DBE=1.

The ineffectiveness of the amine-based inhibitor B to prevent asphaltene precipitation in Oil A may be related to the high relative abundance of $\text{O}_2$ species (carboxylic acids) in Oil A. Acid-base interactions of these acidic species with the basic inhibitor may preclude the inhibitor from interactions with asphaltenes. Based on this
rationale, protic inhibitor A would not interact with the carboxylic acids and would be free to interact with asphaltenes in Oil A.

**Positive-Ion ESI FT-ICR MS of Whole Crude Oils**

Basic species found in petroleum samples have also been extensively characterized by positive-ion ESI FT-ICR MS. Heteroatomic classes observed in positive-ion ESI FT-ICR MS typically include \( N_1, N_1O_1, \) and \( N_1S_1 \) (basic nitrogen, i.e. pyridinic type nitrogen) and \( S_\times O_\times \) classes, presumably sulfoxide type moieties. The crude oils were analyzed by positive-ion ESI FT-ICR to access the role of these basic species in the asphaltene inhibitor chemistry. Figure 7.5 shows the class analysis (heteroatom content) derived from positive-ion ESI FT-ICR MS. Oil A contains higher relative abundance of \( S_\times O_\times \) species (sulfoxides) than Oil B, whereas Oil B has a higher relative abundance of multi-heteroatom containing classes such as \( N_1S_1, N_1O_1 \) and \( N_2 \), which is consistent with the negative-ion class analysis. Isoabundance color-coded contours for plots of DBE versus the carbon number for the \( N_1S_1 \) class are show in Figure 7.6. Oil A has a slightly higher carbon number distribution, from 22-60 versus 19-57 for Oil B. Oil B has a higher relative abundance of higher DBE species than Oil A and both oils have a DBE range from 5-28. Nevertheless, the basic species in both crude oils are very similar, and is also seen in the other classes from negative-ion ESI FT-ICR MS (data not shown).
Crude Oil Positive-ion ESI FT-ICR MS: Class Analysis

Figure 7.5: Heteroatom class distribution (heteroatom content) for selected classes of Oil A and Oil B, derived from high-resolution positive-ion ESI FT-ICR mass spectra. Basic species are similar for both crude oils. Oil A has a higher relative abundance of S\textsubscript{X}O\textsubscript{X} classes, whereas Oil B has a higher relative abundance of multi-heteroatom containing basic nitrogen (pyridinic) species.

Crude Oil Positive-ion ESI FT-ICR MS: N\textsubscript{1}S\textsubscript{1} Class

Figure 7.6: Color-coded isoabundance contours for plots of double bond equivalents (DBE) vs. carbon number for the N\textsubscript{1}S\textsubscript{1} class of Oil A and Oil B, derived from the data shown in Fig. 5. The basic species for both crude oils are very similar, but Oil B shows higher relative abundance of higher DBE species than Oil A.
Negative-Ion ESI FT-ICR MS of Precipitated Asphaltenes

The class analysis derived from negative-ion ESI FT-ICR MS of the precipitated heptane asphaltenes is shown in Figure 7.7.

**Asphaltene Negative-Ion ESI FT-ICR MS: Class Analysis**

Figure 7.7: Heteroatom class distribution (heteroatom content) for selected classes of precipitated asphaltenes from Oil A and Oil B, derived from high-resolution negative-ion ESI FT-ICR mass spectra. Oil B asphaltenes have a high relative abundance of $S_xO_x$ species. These highly polar, proton-donating asphaltenes are expected to interact more strongly with the amine-based inhibitor B than the protic inhibitor A.

Unlike the whole crude negative-ion ESI class analysis, Oil A asphaltenes have a higher relative abundance of nitrogen containing species ($N_1$, $N_1S_1$ and $N_1O_1$) than Oil B asphaltenes. The asphaltene from Oil A also have a higher relative abundance of $O_2$ species (and also $O_3$ and $O_4$) than Oil B asphaltene, which is consistent with the whole crude oil class analysis (see Fig. 7.3). Oil B asphaltenes have higher relative abundance of $S_xO_x$ classes than Oil A asphaltenes, especially the $S_1O_4$ class. The stronger carbonyl IR band for Oil B (see Fig. 7.4) is likely due to the $S_1O_4$ class.
Figure 7.8 shows isoabundance color-coded contours for plots of DBE versus the carbon number for the S$_1$O$_4$ asphaltene class. Figure 8 suggests most of the S$_1$O$_4$ species have low aromaticity, with the highest relative abundance species at DBEs of 1 and 5. Oil B has much higher DBE values, up to 21, versus only up to DBE 15 for Oil A. However, the carbon number distribution is nearly identical from ~10-45. These S$_1$O$_4$ asphaltenes are thought to be highly polar and proton-donating and thus would be expected to interact more strongly with the basic amine-based inhibitor B rather than the protic inhibitor A.

![Graph showing isoabundance color-coded contours for plots of DBE vs. carbon number for the S$_1$O$_4$ asphaltene class from Oil A and Oil B.](image)

Figure 7.8: Color-coded isoabundance contours for plots of double bond equivalents (DBE) vs. carbon number for the S$_1$O$_4$ class for the precipitated asphaltenes from Oil A and Oil B, derived from the data shown in Fig. 7.7. The asphaltenes from Oil B show higher relative abundance of S$_1$O$_4$ species than the asphaltenes of Oil A. Species of 5 DBE have the highest relative abundance.
Positive-Ion ESI FT-ICR MS of Precipitated Asphaltenes

The class analysis for the asphaltenes derived from positive-ion ESI FT-ICR MS (Figure 7.9) is very similar to that of the whole crude oils (compare Fig. 7.5 and Fig. 7.9).

Figure 7.9: Heteroatom class distribution (heteroatom content) for selected classes of precipitated asphaltenes from Oil A and Oil B, derived from high-resolution positive-ion ESI FT-ICR mass spectra. Oil B has higher relative abundance of basic (pyridinic) nitrogen species and multi-heteroatom basic nitrogen species.

Oil B asphaltenes have a higher relative abundance of basic (pyridinic) nitrogen species and multi-heteroatom basic nitrogen species than Oil A asphaltenes. Isoabundance color-coded contours for plots of DBE versus the carbon number for the basic N₁ asphaltene class are shown in Figure 7.10. Like the basic crude oil species (see Fig. 7.6), those from the asphaltenes are very similar. The carbon number distributions range
from ~25-60 and DBEs extend from 5 to 24 for the asphaltenes from Oil A and up to 28 from Oil B asphaltenes.

**Asphaltene Positive ESI FT-ICR MS: N₄ Class**

Figure 7.10: Color-coded isoabundance contours for plots of double bond equivalents (DBE) vs. carbon number for the N₄ class for the precipitated asphaltenes from Oil A and Oil B, derived from the data shown in Fig. 7.9. Like the crude oils (see Fig. 7.5), the basic species in the asphaltenes are very similar, but the asphaltenes from Oil B show somewhat higher DBE values than the asphaltenes from Oil A.

**Conclusions**

Oil-specific asphaltene inhibitor chemistries are well known in the petroleum industry. However, the highly guarded nature of proprietary formulations dose not allow structural/composition level experiments to probe inhibitor-asphaltene chemistries. The current sample set, combined with the high mass accuracy and ultra-high mass resolving power of FT-ICR MS, allowed a unique opportunity to correlate oil-specific asphaltene inhibition to detailed molecular composition of the parent crude oils and their associated asphaltenes. Centrifuge heptane precipitation tests showed oil-specific asphaltene inhibitor performance;
inhibitor A is specific to Oil A, and inhibitor B to Oil B. However, total acid number (TAN), elemental analyses and FT-IR data were similar for both crude oils.

Negative-ion ESI FT-ICR MS identifies a high relative abundance of non-aromatic $O_2$ species in Oil A, whereas Oil B contains a higher relative abundance of neutral nitrogen containing species than Oil A. The ineffectiveness of amine-based inhibitor B to prevent asphaltene precipitation in Oil A may result from acid-base interactions between the inhibitor and carboxylic acids, rather than the asphaltenes. Similarly, protic inhibitor A would not interact with acidic species in Oil A and therefore be free to interact with asphaltenes. The results provide evidence that the effectiveness of inhibitor A can be linked to the class and type speciation for the polar species identified by FT-ICR MS.

Positive-ion ESI FT-ICR MS of isolated asphaltenes yields slightly higher relative abundance of basic nitrogen species in Oil B over Oil A. However, negative-ion ESI FT-ICR MS of the asphaltenes shows a high relative abundance of $S_1O_4$ species in Oil B. These highly polar, proton-donating asphaltenes are expected to interact more strongly with the amine-based inhibitor B than the protic inhibitor A. Again, the results suggest that the effectiveness of the inhibitor can be explained by the polar species identified by ESI FT-ICR MS.
CHAPTER 8.
CARRYOVER IN A SARA FRACTIONATED ARABIAN MEDIUM CRUDE OIL CHARACTERIZED BY FIELD DESORPTION IONIZATION, NEGATIVE-ION AND POSITIVE-ION ELECTROSpray IONIZATION FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

Summary

We present field desorption and negative/positive-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry of a SARA (saturate, aromatic, resin, asphaltene) fractionated Arabian medium crude oil. Class analysis is consistent between the three ionization methods; the aromatic fraction contains the highest relative abundance of nitrogen species and the resin fraction contains the highest relative abundance of oxygen species. All ionization methods show compositional bleed between fractions, especially between the parent crude oil, saturate and aromatic fractions, and between the resin and asphaltene fractions. SARA fractionation facilitates identification of aromatic species not observed in the parent crude oil.

Introduction

The combination of saturated and unsaturated hydrocarbons, polar compounds with nitrogen, sulfur and oxygen heteroatoms, and metals makes characterization of individual species in bulk crude oil extremely difficult. The saturate/aromatic/resin/asphaltene (SARA) chromatographic method is commonly used to separate crude oils based on their polarity/solubility. Open column chromatography separations are common, however high performance liquid chromatography (HPLC) SARA fractionation has also become popular.179-182

Saturated hydrocarbons have been partially characterized by gas chromatography mass spectrometry (GC – MS)183 and two dimensional gas chromatography mass spectrometry (GC x GC MS).184 The resin
fraction has been analyzed by low resolution electrospray mass spectrometry (ESI – MS)\textsuperscript{185} and the asphaltene fraction has been extensively characterized\textsuperscript{144}. In addition, vibrational spectroscopy has been used to characterize all fractions\textsuperscript{180, 181}. The aromatic fraction of a South American crude oil has been characterized by positive-ion ESI FT-ICR MS\textsuperscript{186}.

The ultra-high resolving power (m/\(\Delta m_{50\%}\) > 350,000 (in which \(\Delta m_{50\%}\) is the magnitude mode mass spectral full width at half-maximum peak height)) and high mass accuracy (typically < 500 ppb) of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) allows the assignment of a unique elemental composition for each peak in the mass spectrum. Field desorption (FD) FT-ICR MS ionizes hydrocarbons and non-polar sulfur not accessible by electrospray ionization (ESI)\textsuperscript{28, 29}. ESI FT-ICR MS preferentially ionizes acids/bases in the negative-ion\textsuperscript{43, 74, 96} and positive-ion modes\textsuperscript{18, 75}. Together, the three methods yield a great deal of compositional information about the crude oil. The high mass resolving power of our 9.4 T electrospray\textsuperscript{53} and field desorption\textsuperscript{29} mass spectrometers resolve species differing in elemental composition by C\textsubscript{3} versus S\textsubscript{1}H\textsubscript{4} (0.0034 Da), a common doublet in crude oil mass spectra.

Here, we report the first characterization of an Arabian medium crude oil and its SARA fractions by FD and negative/positive-ion ESI FT-ICR MS. Elemental composition assignment allows the organization of observed compounds by class (heteroatom content), type (double bond equivalents, the number of rings and/or double bonds (DBE)) and carbon number. Isoabundance color-coded plots for DBE versus the carbon number present a unique fingerprint for each fraction and aid data interpretation. We describe heteroatom content and compositional change between fractions for non-polar and polar species and illustrate extensive carryover for an open-column SARA fractionation.
Experimental Methods

Sample Description and SARA Fractionation

An Arabian medium crude oil was supplied by ExxonMobil (Annandale, NJ). The SARA method was used to fractionate the crude oil into saturate, aromatic, resin and asphaltene fractions. Approximately 1 gram of crude oil was dissolved into 40 mL of hexanes. Precipitated asphaltenes were filtered with Whatman #2 paper and the supernatant was concentrated in ~10 mL of hexanes and adsorbed onto 6 g of alumina. The alumina was dried under nitrogen then packed on top of 20 g of neutral alumina in an 11 x 300 mm column. The saturate fraction was eluted with 80 mL of hexanes, the aromatic fraction with 150 mL of toluene and the resin fraction with 100 mL of toluene:methanol (80:20, v/v).

Field Desorption FT-ICR MS

Samples for field desorption MS were prepared to 1 mg/mL in methylene chloride and used without additional modification. Field desorption analyses were performed on a custom built 9.4 Tesla FT-ICR mass spectrometer described in Chapter 1. Ions are generated externally with a commercial field desorption ionization source (Linden CMS, Leeste, Germany). Instrument control, data acquisition and data analysis were controlled by a MIDAS data station.

Electrospray Ionization FT-ICR MS

All electrospray FT-ICR MS experiments were performed on the 9.4 T ESI FT-ICR mass spectrometer described in Chapter 1. Electrospray samples were prepared to 1 mg/mL in 50:50 (v/v) toluene:methanol. To ensure efficient ionization, 1% ammonium hydroxide or acetic acid was
added for negative or positive ion electrospray (~65 fM). All solvents were HPLC grade (Fisher Scientific, Pittsburgh, PA).

**Mass Calibration and Data Analysis**

Field desorption spectra were internally calibrated on the alkybenzene homologous series as reported previously.\textsuperscript{29} ESI FT-ICR mass spectra were internally calibrated with respect to a high relative abundance (O\textsubscript{2}, negative-ion mode/N\textsubscript{1}, positive-ion mode) homologous series present in each sample for negative/positive electrospray as previously described.\textsuperscript{74, 75}

Mass values for singly charged ions between 225-1000 Da with a relative abundance greater than eight times the standard deviation of the baseline noise (8\textsigma) were converted from IUPAC mass scale to the Kendrick mass scale\textsuperscript{19} and sorted by Kendrick mass defect values to facilitate identification of homologous series.\textsuperscript{20}

**Results and Discussion**

Polar components (NSO containing acids and bases and low-polarity sulfur species) constitute ~ 5-15 % of petroleum products, while non-polar species (e.g. saturated hydrocarbons and aromatic hydrocarbons) constitute the majority (~ 85-95 %).\textsuperscript{42} FD produces true molecular ions, M\textsuperscript{+}, and does not require adduction of a proton or other ion to create a quasimolecular ion. Thus, ions observed by FD represent the most abundant species in complex petroleum mixtures; which tend to be found in limited, specific carbon number and DBE ranges. ESI selectively ionizes the less abundant polar components of petroleum with high specificity; typically across a broad mass range (200 < m/z < 1,000).
**Field Desorption Ionization FT-ICR MS**

*Figure 8.1* shows the class analysis (heteroatom content) for an Arabian medium crude oil and its SARA fractions derived from field desorption ionization FT-ICR MS.

![Medium Arabian Crude Oil - Class Analysis](image)

*Figure 8.1.*: Heteroatom class distribution (heteroatom content) generated by FD FT-ICR MS analysis of an Arabian medium crude oil.

The crude oil, saturate, aromatic and asphaltene fractions have similar class composition, with the hydrocarbon and $S_1$ classes observed at high relative abundance. The aromatic fraction contains a higher relative abundance of nitrogen than the crude and the other SARA fractions, and is the only fraction to contain $N_1S_1$ species. The resin fraction displays unique behavior with oxygen containing classes $O_2$ and $O_4$ in high relative abundance and $O_1$ and $O_3$ classes enhanced by fractionation.
The asphaltene fraction contains the highest relative abundance of non-polar S\textsubscript{1} species.

**Figure 8.2** shows isoabundance color-coded plots for double bond equivalents versus the carbon number for the hydrocarbon class derived from FD FT-ICR MS mass spectra.

![Figure 8.2: Color-coded isoabundance contour plots of double bond equivalents (DBE) versus the carbon number for the hydrocarbon class from Fig. 8.1 for an Arabian medium crude oil (top, left) and its saturate (top, right), aromatic (bottom, left), resin (bottom, center) and asphaltene (bottom, right) fractions.](image)

The parent crude (Fig. 8.2, top left) shows high relative abundance for non-aromatic hydrocarbons with a DBE of 2 and carbon numbers from 17-47. In addition, species with DBE of 4 (likely alkylbenzenes) and carbon numbers from 27-39 also have high relative abundance. Higher aromatic species (DBE > 7) display narrower carbon number
distributions than lower DBE species. The saturate fraction plot (Fig. 8.2, top right) shows that the DBE and carbon number distributions for hydrocarbon species are very similar to those found in the parent crude oil. SARA fractionation allows for the identification of highly aromatic hydrocarbons in the aromatic fraction (Fig. 8.2, bottom left) that are not observed in the parent crude oil. The resin fraction (Fig. 8.2, bottom middle) contains a low overall abundance of hydrocarbons (see Fig. 8.1). However, a few hydrocarbon species are observed in the resin at high relative abundance; DBE 2 and 3 between carbon numbers 20-24. Higher aromaticity hydrocarbons are also observed in the asphaltene fraction (Fig. 8.2, bottom right). The asphaltene fraction shows the highest carbon number species (up to 50 carbon atoms).

**Figure 8.3** shows $S_1$ class isoabundance color-coded plots for DBE versus the carbon number as revealed by FD FT-ICR MS. The parent crude oil (Fig. 8.3, top left) contains high relative abundance species at DBE of 6 with a carbon number range of 30-37, consistent with a possible structure of a benzo-thiophenic core with alkyl side chains. Lower relative abundance species extend up to DBE of 14 as is the case for the saturate fraction. The saturate fraction (Fig. 8.3, top right) shows the same DBE 6 species with highest relative abundance. The aromatic fraction (Fig. 8.3, bottom left) also contains DBE 6 species in high relative abundance and shows enhancement of more aromatic species. Like the hydrocarbon class aromatic fraction (Fig 8.2., bottom left), the $S_1$ class shows an additional area of high relative abundance with higher aromaticity (DBE 12-16) and carbon number 22-30 (species that were not observed in the parent crude oil). The resin fraction shows low overall abundance of sulfur containing species. The asphaltenes (Fig. 8.3, bottom right) contain the same high relative abundance DBE 6 species as the crude, saturate and aromatic fractions, and also show higher aromatic species not observed in the parent crude oil. Non-
aromatic species with DBE 1-5 suggest co-precipitation of resins in the asphaltene fraction.

Figure 8.3: Color-coded isoabundance contour plots for plots of double bond equivalents (DBE) versus the carbon number for the S₁ class of Fig. 8.1 for an Arabian medium crude oil (top, left) and its saturate (top, right), aromatic (bottom, left), resin (bottom, center) and asphaltene (bottom, right) fractions.

Figures 8.2 and 8.3 illustrate both the advantage of group-type fractionation prior to FD FT-ICR MS as well as compositional bleed among SARA fractions. Without fractionation, the hydrocarbons observed are limited to those that have similar composition to the saturate fraction. Similarly, S₁ species with low aromaticity (< 6) and high aromaticity (> 14) are absent from the parent crude oil spectrum. More aromatic hydrocarbons and S₁ species with high relative abundance in the aromatic and asphaltene fraction are not observed in
the parent crude oil. In addition to carryover between fractions, resin co-
precipitation in the asphaltenes is observed for the S₁ species.

**Negative-Ion ESI FT-ICR MS**

*Figure 8.4* shows negative-ion ESI FT-ICR MS class analysis (heteroatom content) for Arabian medium crude oil and its aromatic, resin and asphaltene fractions. Electrospray ionization of the saturate fraction did not yield sufficient ion signal for FT-ICR MS analysis for either polarity. The parent crude and all fractions contain the O₂ class in highest relative abundance, except the aromatic fraction, which contains the N₁ class in highest relative abundance. The parent crude oil contains a wide range of nitrogen, sulfur and oxygen (N, S, O) heteroatom containing acidic species. SARA fractionation allows for the identification of solubility dependent class distributions for the aromatic, resin and asphaltene fractions. The N₁ class has high relative abundance in the aromatic fraction; in agreement with FD FT-ICR MS class analysis (see Fig. 8.1). In addition, the aromatic fraction contains the O₁ class (possibly phenolic species) in high relative abundance and multi-functional nitrogen containing classes (N₁O₁, N₁O₂, N₁S₁) and oxygen containing classes (O₂, O₃, O₄, S₁O₁ and S₁O₃) in low relative abundance. The resin fraction contains many oxygen containing classes (O₁, O₂, O₃, O₄, O₆, O₇, S₁O₃, S₁O₄, and N₂O₂), again in good agreement with FD FT-ICR MS class analysis (Fig. 8.1). Nitrogen containing classes are almost completely absent in the resin fraction, except for low relative abundance of the N₂O₂ class. The asphaltene fraction contains a wide distribution of NSO compounds, with high relative abundance classes O₂ and N₁ and lower relative abundance multi-functional classes such as N₁S₁, S₁O₃, S₁O₄, N₁O₂, N₂O₂, N₁S₂, O₁, O₃, O₄, O₅, O₆ and O₇.
Medium Arabian Crude Oil - Class Analysis
Negative-Ion ESI FT-ICR MS

Figure 8.4: Heteroatom class distribution (heteroatom content) derived from negative-ion ESI FT-ICR MS analysis of an Arabian medium crude oil.

The isoabundance color-coded plots for the O₂ class (Figure 8.5) show bleed between all SARA fractions. The parent crude oil and the three fractions all have high relative abundance of non-aromatic O₂ species with DBE of one and two and with low carbon number (16-20). Low abundance O₂ species are similar for the crude oil, resin and asphaltene fractions, with DBE from 1-13 and 15-50 carbons. The aromatic fraction has low overall abundance of O₂ species (see Fig. 8.4) and an absence of high DBE/high carbon number species.
Figure 8.5: Color-coded isoabundance contour plots for double bond equivalents (DBE) versus the number for the O\textsubscript{2} class of Fig. 8.4 for an Arabian medium crude oil (top, left) and its aromatic (top, right), resin (bottom, left) and asphaltene (bottom, right) fractions.

**Figure 8.6** shows isoabundance color-coded plots for the N\textsubscript{1} class by negative-ion ESI FT-ICR MS. The parent crude oil, aromatic and asphaltene fractions all show similar nitrogen composition. The resin fraction did not contain any acidic N\textsubscript{1} species. DBE values range from 9-22 for the aromatic and asphaltene fraction and up to 24 for the parent crude oil. Carbon numbers range from ~ 19-55 and narrow as aromaticity increases. Two areas of high relative abundance indicate two stable core structures for the neutral N\textsubscript{1} species. The first, with DBE 9-10 is consistent with the possible structure of a carbazole core with alkyl side chains. The sharp cutoff at DBE 9 indicates acidic N\textsubscript{1} species with DBE 9 are most stable in this crude oil. The addition of a benzene ring to this core yields a DBE of 12, where the second area of high relative
abundance is centered. The asphaltene fraction shows a wider carbon number distribution for the more aromatic species, which extends from 23-42.

![Figure 8.6: Color-coded isoabundance contour plots for plots of double bond equivalents (DBE) versus the carbon number for the N₁ class of Fig. 8.4 for an Arabian medium crude oil (top, left) and its aromatic (top, right), resin (bottom, left) and asphaltene (bottom, right) fractions. The resin fraction did not contain N₁ species.](image)

Additional acidic species also show large compositional bleed between fractions. Observed N₁S₁ species are similar for the crude oil, aromatic, and asphaltene fractions and the resin fraction does not contain N₁S₁ species (data not shown). The crude oil contains a large distribution of S₁O₃ species (DBE 0-10 and C# 15-45), with the highest relative abundance species at DBE 4 with 15-20 carbons. The high relative abundance species are observed in the aromatic, resin and asphaltene fractions, with slightly more aromatic S₁O₃ species in the asphaltene fraction (data not shown).
Figure 8.7 shows positive-ion ESI FT-ICR MS class analysis (heteroatom content) for Arabian medium crude oil and its aromatic, resin and asphaltene fractions.

Figure 8.7: Heteroatom class distribution (heteroatom content) for an Arabian medium crude oil derived from positive-Ion ESI FT-ICR MS.

The positive-ion spectra contain high relative abundance of basic N\textsubscript{\text{X}} classes (pyridinic nitrogen), followed by N\textsubscript{\text{X}}O\textsubscript{\text{X}}, N\textsubscript{\text{X}}S\textsubscript{\text{X}} and S\textsubscript{\text{X}}O\textsubscript{\text{X}} (sulfoxides). The parent crude oil has high relative abundance of N\textsubscript{1} and N\textsubscript{1}S\textsubscript{1} classes and other multi-hetero atom containing classes in low relative abundance. The aromatic fraction shows the highest relative abundance of N\textsubscript{1} species, in agreement with FD and negative-ion FT-ICR MS class analyses (see Fig. 8.1 and Fig. 8.4). The N\textsubscript{1}S\textsubscript{1} class has the second
highest relative abundance and low relative abundance multi-heteroatom classes are present. Salt adducts (in the form of $S_xO_xNa$) are seen in high relative abundance in the resin fraction, whereas $N_1$ species are present in low relative abundance. The resin fraction also contains low relative abundance of multi-heteroatom containing classes. The class distribution of the asphaltene fraction is very similar to the parent crude.

Isoabundance color-coded plots for the $N_1$, $N_1O_1$ and $N_1S_1$ have similar trends, so only the $N_1$ class (Figure 8.8) is presented. Isoabundance color-coded plots of DBE versus the carbon number in Figure 8.8 indicate very similar composition of basic nitrogen in all fractions. DBE values range from ~4-28 for the parent crude oil (Fig. 8.8, top left) and asphaltene fraction (Fig. 8.8, bottom right), whereas the aromatic (Fig. 8.8, top right) and resin (Fig. 8.8, bottom left) fractions only extend to DBE 24. All fractions have species with high relative abundance at DBE 8-12. The resin fraction has a low relative abundance of basic $N_1$ species, with a more narrow carbon number distribution (~20-45) than the parent crude, aromatic and asphaltene fractions (~22-55). Low relative abundance of highly aromatic basic $N_1$ species in the resin fraction may be caused by formation of aggregates with the highly abundant low DBE $O_2$ acidic species, which may carry the $N_1$ species from the aromatic to the resin fraction. Additional evidence for this occurrence is supported by previous aggregation studies performed by both low resolution and high resolution mass spectrometry (see Chapter 6).\textsuperscript{109}
Figure 8.8: Color-coded isoabundance contour plots for plots of double bond equivalents (DBE) versus the carbon number for the N1 class of Fig. 8.7 for an Arabian medium crude oil (top, left) and its aromatic (top, right), resin (bottom, left) and asphaltene (bottom, right) fractions.

Conclusions

The present work uses ultra-high resolution field desorption ionization and negative/positive-ion electrospray FT-ICR MS to characterize the composition of an Arabian medium crude oil and its column separated SARA fractions. Heteroatom class trends are consistent between the three ionization methods. Field desorption ionization identifies highly aromatic non-polar species not observed in the parent crude oil in the aromatic and asphaltene fractions. The resin fraction shows low relative abundance of hydrocarbons and non-polar sulfur. In addition, analysis of only the parent crude oil yields heteroatom content and class composition most like the saturate
fraction. Similar composition suggests significant bleed between fractions and resin co-precipitation in the asphaltene fraction is observed.

Electrospray ionization results also indicate that changes in aromaticity between fractions are seen for aromatic nitrogen by both ESI methods. Unlike FD FT-ICR MS, analysis of only the parent crude oil yields heteroatom and class compositions similar to the asphaltene fraction. The compositional similarity between fractions suggests a more comprehensive method for the characterization of crude oils and derived liquids may be needed.
APPENDIX A.

Compositional Analysis of Acidic Species in Athabasca Bitumen and Their Effect on Oil Sand Ore Processability

The water-based extraction methods for recovery of bitumen from “good” oil sands ore can be very successful, with a total bitumen recovery over 93%. However, the processability of bitumen ore depends on a number of factors which include fines content, divalent cation content and the degree of weathering (age). Typically, a high grade ore (high bitumen and low fines content) posses good processability, whereas low-grade ores (high fines and low bitumen content) are more difficult to process. In this study, the acidic organic species from extracted bitumen from a “good” ore (12.7% recovery) and a “bad” ore (6.2% recovery) were analyzed by negative-ion ESI FT-ICR MS to determine molecular composition effects on processability.

Figure A.1 shows the heteroatom class analysis (heteroatom content) for selected classes for the “good” and “bad” ore bitumen. The heteroatom content for both ores is very similar. The most abundant classes are similar to those from the bitumen analyzed in Chapter 3; the O$_2$ class has the highest relative abundance followed by the S$_2$O$_2$ class.

Isoabundance color-coded contours for plots of DBE versus the carbon number for the O$_2$ class and S$_1$O$_2$ class are shown in Figures A.2 and A.3. The O$_2$ class has a high relative abundance of DBE = 3 species, consistent with the bitumen studies in Chapter 3. The similarity of the contour plots suggest the organic acid composition does not account for differences in ore processability. Precipitated asphaltenes from both ores were also analyzed, with no significant differences in organic acid composition found (data not shown).
Figure A.1: Heteroatom class distribution (heteroatom content) for selected classes of a “good” and “bad” bitumen ore derived from negative-ion ESI FT-ICR MS. The heteroatom content is very similar for both ores. The $O_2$ class (naphthenic acids) has the highest relative abundance, followed by the $S_1O_2$ class.
Figure A.2: Color-coded isoabundance contour for a plot of DBE versus the carbon number for the O$_2$ class (naphthenic acids) of “good” and “bad” Athabasca bitumen ore.
Figure A.3: Color-coded isoabundance contour for a plot of DBE versus the carbon number for the $S_1O_2$ class of “good” and “bad” Athabasca bitumen ore.
APPENDIX B.

Compositional Analysis of Emulsion Bound Bitumen and Treated Bitumen by Negative-ion ESI FT-ICR MS

The water extraction method for the recovery of bitumen from oil sands often results in the formation of emulsions. The formation of these emulsions decrease bitumen recovery, reduces process efficiency and ultimately increase the process cost and lead to revenue loss. It has been shown by negative/positive-ion ESI FT-ICR MS that the composition of the organic species does play a role in bitumen emulsion formation. In this study we have analyzed the bitumen component of a water/oil emulsion and a treated bitumen sample that did not form an emulsion by negative-ion ESI FT-ICR MS to determine the effect of acidic organic species on emulsion formation.

The water from the bitumen emulsion was decanted into a 500 mL round-bottom flask into which ~200 mL of toluene was added. The toluene was evaporated on a rotary-evaporator and the process was repeated four times. A brown residue with some solid particulates remained in the round bottom flask after the fourth evaporation. The residue was re-dissolved in toluene and analyzed as detailed in Chapter 1.

Figure B.1 shows the heteroatom class analysis (heteroatom content) for selected classes for the treated bitumen and the isolated emulsion material. The material isolated from the emulsion shows higher relative abundance of more water-soluble classes N\textsubscript{1}O\textsubscript{2}, O\textsubscript{2} and O\textsubscript{4} than the bitumen, consistent with findings that suggest oxygenated functional groups promote aqueous solubility. Further, all classes detected in the isolated emulsion material contain at least 2 oxygen atoms.
Figure B.1: Heteroatom class distribution (heteroatom content) for selected classes of treated bitumen and isolated emulsion material derived from negative-ion ESI FT-ICR MS. The isolated emulsion material contains only classes with 2 or more oxygen atoms.

Figures B.2 and B.3 show isoabundance color-coded contours for plots of DBE versus the carbon number for the O_2 class and N_1 class for the treated bitumen and the emulsion bitumen. The similarity suggests the chemical composition of the organic acids does not play a large role in emulsion formation. However, the amount of water-soluble organic acids may contribute (see Fig. B.1), as well as other factors such as inorganic species.
Figure B.2: Color-coded isoabundance contour for a plot of DBE versus the carbon number for the $O_2$ class (naphthenic acids) of a treated bitumen sample and the bitumen isolated from a water/oil emulsion.
Figure B.3: Color-coded isoabundance contour for a plot of DBE versus the carbon number for the N$_1$ class (pyrrolic nitrogen) of a treated bitumen sample and the bitumen isolated from a water/oil emulsion.
APPENDIX C.

Sample Handling Effects on Petroleum ESI FT-ICR Mass Spectra

Mass spectral analysis is typically done on “dead” oil samples, that is, oil that is no longer under the pressure and temperature encountered in the reservoir. Non-reservoir samples are typically sampled and stored in glass vials until analysis and the consequences of short-term and long-term storage are not known, as are the effects of different storage conditions (e.g. stored in solvent or exposed to atmosphere). In addition, it is unknown if the electrospray ionization process effects the chemical composition of crude oil samples. Oxidation or nitrogenation due to atmospheric oxygen and nitrogen present in the electrospray process has not been studied. The hot tapped samples acquired for this study allow both sample handling and electrospray issues to be studies on samples that have not been exposed to atmosphere since the start of the refining process.

Figure C.1 shows heteroatom class analysis (heteroatom content) for hot tapped Athabasca Canadian bitumen collected and analyzed under inert conditions (Bitumen O$_2$ Free), aspirated with air for 3.5 hours (Bitumen Bubbled), stored in ambient conditions for 8 months (Bitumen 8 Month Exposure) and the aspirated sample stored in toluene for 8 months (Bitumen Bubbled, TOL 8 Months) derived from negative-ion ESI FT-ICR MS. The bitumen O$_2$ free and aspirated bitumen were both analyzed under inert electrospray conditions to identify oxidation due only to the aspiration and not electrospray. The aspirated bitumen has slightly higher relative abundance of O$_1$ and O$_2$ species over the bitumen that was analyzed under inert conditions, which suggests only little oxidation due to aspiration with ambient air. The raw bitumen exposed to ambient air for 8 months shows minor class differences from the inert ESI bitumen. The 8 month exposed sample shows almost total depletion of the multiple oxygen classes O$_4$ and O$_5$. There is little change
in the relative abundance of the O\textsubscript{2} class and a slight increase in the O\textsubscript{1} class, an indication of only slight oxidation. The increase in N\textsubscript{1} relative abundance may be nitrogenation, but it is likely a relative increase due to the loss of the higher oxygen containing classes. The aspirated sample stored in toluene for 8 months is very similar to the original aspirated bitumen. It shows depletion of the O\textsubscript{5} class and a slight increase in the O\textsubscript{2} class. To further investigate these changes in heteroatom content, iso-abundance color coded plots of DBE versus the carbon number where created to examine changes in chemical speciation.

Figure C.1: Negative-ion ESI FT-ICR MS derived heteroatom class distribution (heteroatom content) for Athabasca bitumen with various sample handling and storage conditions.

Color-coded isoabundance contours for plots of DBE versus the carbon number for the O\textsubscript{2}, S\textsubscript{1}O\textsubscript{2}, N\textsubscript{1}O\textsubscript{2} and N\textsubscript{1} classes from the negative-ion ESI FT-ICR MS data shown in Fig. 7.1 are shown in Figure C.2.
Figure C.2: Color-coded isoabundance contours for plots of DBE versus the carbon number for the O$_2$, S$_1$O$_2$, and the N$_1$O$_2$ classes derived from the data shown in Fig. 7.1.

The bitumen exposed to ambient atmosphere shows a slight depletion of lower carbon number species in all classes, with the highest relative abundance species also shifting to somewhat higher carbon numbers.
The other storage conditions show little compositional change. Other heteroatom classes exhibit the same trends as seen in Fig. C.2.

The heteroatom class analysis (heteroatom content) derived from positive-ion ESI FT-ICR MS is shown in Figure C.3. The O$_2$ free and aspirated samples are very similar, which indicates little or no nitrogenation/oxidation of basic species. Both 8 month samples exhibit a decrease in relative abundance of N$_1$ species and a relative increase in S$_X$O$_X$ species (sulfoxides, see inset in Fig. C.3). The appearance of these sulfoxide species may be due to auto-oxidation of sulfides, which is known to occur in fossil fuels.$^{194}$

![Figure C.3: Positive-ESI FT-ICR MS derived heteroatom class distribution (heteroatom content) for Athabasca bitumen with various sample handling and storage conditions. Inset shows selected S$_X$O$_X$ classes in greater detail.](image-url)
Figure C.4 shows color-coded isoabundance contours for plots of DBE versus the carbon number for the N$_1$, N$_1$S$_1$ and N$_1$O$_1$ classes derived from the positive-ion ESI FT-ICR MS data shown in Fig. C.3.
The speciation of basic nitrogen for the O$_2$ free and aspirated samples are nearly identical. However, both 8 month samples display a shift to higher carbon number, unlike the acidic species that only displayed this shift for the samples exposed to ambient atmosphere.

Analysis of petroleum samples by ESI mass spectrometry has become popular in many research labs. However, up to this point little was known about the consequences of different handling of the samples before analysis. Athabasca bitumen collected directly from the refinery was prepared and electrosprayed under an inert atmosphere. Upon comparison with a sample aspirated with air for 8 hours, few compositional differences were observed. Negative ESI FT-ICR MS showed aspiration yielded slightly higher relative abundance of O$_1$ and O$_2$ species, possibly an indication of slight oxidation. When exposed to ambient atmosphere for 8 months, the higher oxygen containing classes O$_4$ and O$_5$ are depleted, and the N$_1$ class increases in relative abundance; likely due to the loss of the oxygen species. The aspirated sample stored in toluene for 8 months shows few differences from the original aspirated sample. Color-coded isoabundance contours for plots of DBE versus the carbon number for negative-ion classes show a slight increase to higher carbon number for the bitumen exposed to ambient atmosphere for 8 months. No other changes in acidic speciation are observed. Positive ESI FT-ICR MS class analysis shows an increase in some S$_x$O$_x$ classes in both samples analyzed after 8 months, likely due to the oxidation of sulfides to sulfoxides. In addition, both 8 month samples show a shift to higher carbon number. However, there is little change to the DBE distribution, thus the core structure of the molecules.

The results of this study suggest the composition of polar species change little with different sample handling conditions. It is not necessary to go to extreme lengths to limit expose to atmosphere during sample preparation or during the electrospray process. However,
prolonged exposure to ambient atmosphere or storage in toluene should be avoided to limit auto-oxidation reactions.
Appendix D.

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