

### **Innovations and developments in bitumen composition analysis**

*Jeramie Adams, Joe Rovani, Ryan Boysen, Michael Elwardany, Jean-Pascal Planche  
Western Research Institute*

#### **Abstract**

The analysis of bitumen composition has always been a challenge because of the complexity and nature of bitumen molecules forming a continuum of associating chemical molecules. The separation by molecule families with similar features, saturates, aromatics, resins and asphaltenes (SARA) became the norm. However, SARA separation was developed mainly for straight run bitumens, and not to account for current changes in refining streams, blends and modification processes. Recently the Western Research Institute invented a new separation combining chromatography with solubility called SAR-AD™ that separates saturates, aromatics and resins by liquid chromatography, and asphaltenes by solubility in solvents with increasing polarity. This technique provides eight fractions specifically reporting to the four generic ones. This technique is used to characterize a wide variety of binders from around the world, produced using various processes, and allows for obtaining strong correlations between the fractions, the physical properties and aging levels of the bitumens. Recent studies were devoted to better understand the chemical make-up of these fractions, using model compounds to identify molecular classes in the separation. Key compound features cause molecules to report to the chromatographic saturates, aromatics and resins fractions. The saturates fraction was shown to contain saturated hydrocarbons ranging from linear to cyclic species containing naphthenic rings; the aromatics separation produces three different fractions based upon the number of fused aromatic rings; and the resins fraction contains molecules influenced by heteroatoms and functional groups. The size, geometry, and location of aliphatic side chains result in steric hindrance causing molecules to report to different fractions. Similarly, functional groups with heteroatoms can change where the molecules report. Further developments are being made towards a second-generation of the SAR-AD instrument based on multi-dimensional separations and advanced detection techniques. Applications include the identification of additives, special refining processes, and aging. Examples were obtained from samples provided by WRI led Industry consortium's partners.

## INTRODUCTION

In its simplest form, bitumen is the by-product bottoms from the distillation of crude oil, which consequently contains the largest molecules in a highly complex mixture of more than tens of thousands of different molecules. Currently it is not realistic to map the complete genome of each bitumen, although significant strides have been made with advanced mass spectrometry techniques. In order to deal with such a complex mixture, ranging from non-polar molecules to highly aromatic and polar molecules, it is reasonable to take a divide-and-conquer approach by separating bitumen into fractions with similar molecular features and then to understand the chemical structure and function boundaries within these fractions. The most fundamental separation applied to bitumen, and petroleum in general, is the separation of maltenes and asphaltenes by the addition of a light aliphatic solvent. The solvent causes asphaltenes to precipitate—which are the most polar and generally most aromatic fraction—while the solvent-soluble portion is termed the maltenes. Further separation of the maltenes has traditionally been performed using various normal-phase chromatography techniques to separate classes of compounds (saturates, aromatics, resins) by their affinity for adsorption on a stationary phase with elution of fractions using mobile solvent phases of varying solubility parameter and chromatographic strength. When combined with gravimetric data from the asphaltene precipitation, these separations are known generically as saturates, aromatics, resins, asphaltenes (SARA) analyses.

Most SARA separations have a common difficulty in that it is necessary to first precipitate the asphaltenes from the maltenes prior to separating the maltenes by chromatography. This is because asphaltenes irreversibly adsorb to most stationary phases, thus poisoning their activity making them useless for sequential separations. This has been a key factor preventing the widespread use of automated SARA separations for rapid characterization of bitumen. At the Western Research Institute (WRI), this limitation has been overcome using an on-column precipitation and redissolution technology within an HPLC framework, while at the same time providing additional chemically distinct fractionation of the maltenes and asphaltenes. This patented process [1] precipitates asphaltenes with an inert medium allowing the maltenes to travel downstream for further chromatographic separation into one saturates fraction, three aromatics fractions and one resins fraction using three chromatography columns and combinations of solvents. Furthermore, the asphaltenes retained by the inert medium are further separated into three different solubility-based fractions using solvents of increasing solvent strength. This first generation hybrid system—that combines chromatography of the maltenes (SAR) with the solubility separation of the asphaltenes (Asphaltene Determinator™ AD)—is known as the SAR-AD™, and further called the “Separation” in the paper. This repeatable analytical technique is useful for fingerprinting bitumen, tracking aging kinetics, monitoring colloidal stability of bitumen, formulating bitumen, determining the compatibility of blends and additives and is also able to diagnose bitumen that has been treated in a pyrolysis process such as visbreaking/ partial upgrading, catalytic cracking or hydrocracking.

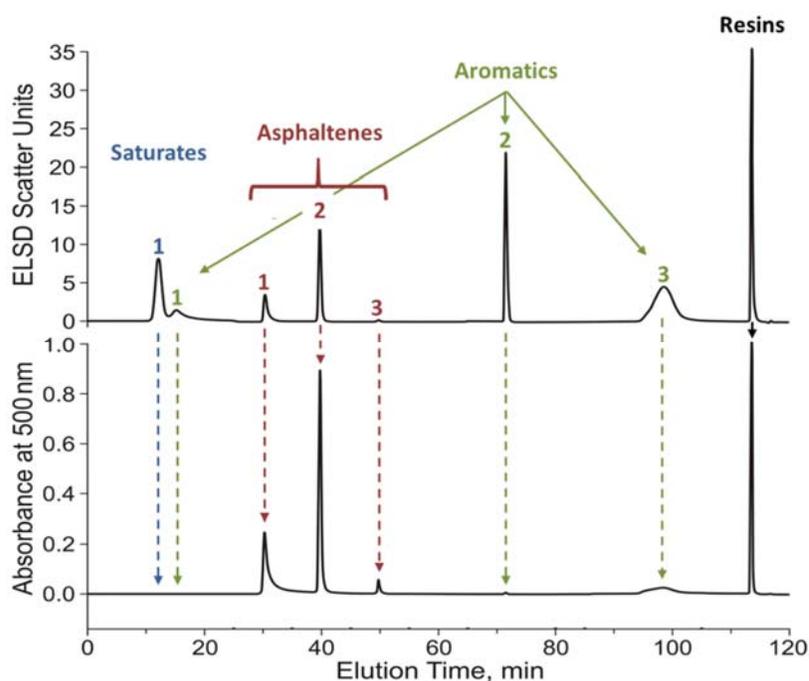
This paper demonstrates some recent examples of the utility of the first generation Separation. Some aspects of the molecules reporting to maltenes are shown to provide chemical distinction between the fractions. Finally some examples are given regarding the second generation Separation which provides additional insight into the various fractions using size exclusion chromatography (SEC), fluorescence spectroscopy (FS) and Fourier transform infrared spectroscopy (FTIR).

The results were obtained on binders provided by partners of the Asphalt Industry Research Consortium (AIRC) and the Heavy Oil Research Consortium (HORC), both initiated by the Western Research Institute (WRI). The AIRC sample base includes over 100 binders from around the world, covering a wide variety of crude sources, most refining and modification processes, including bio-additives.

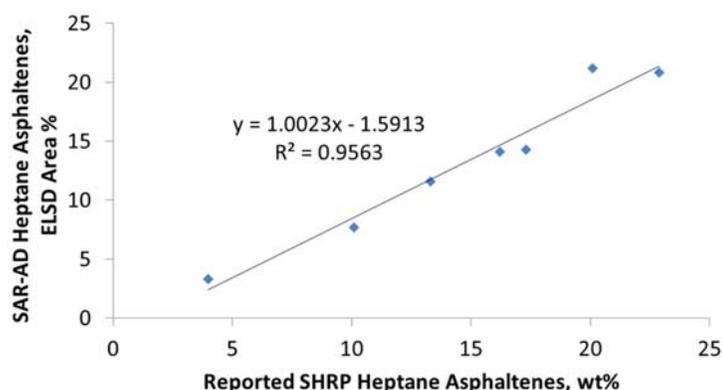
## 1. 1<sup>st</sup> GENERATION SEPARATION AND UTILITY

### 1.1 Separation

In the separation, five distinct maltenes fractions are obtained by chromatography and three different asphaltene subfractions are obtained by solubility (Figure 1) [1]. The separation uses an evaporative light scattering detector (ELSD) which provides data similar to weight percent (Figure 2) and a variable wavelength detector which measures the concentration of coloured materials that absorb light at 500 nm due to the presence of brown chromophores in these fractions.



**Figure 1: Chromatogram of a Lloydminster bitumen. Asphaltene 1 is Cyclohexane-soluble, Asphaltene 2 is Toluene-soluble and Asphaltene 3 is Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>)-soluble.**



**Figure 2: Comparison of heptane-insoluble asphaltene contents between SHRP and Separation data for AAA-1, AAB-1, AAC-1, AAE-1, AAF-1, AAK-1, and AAM-1.**

## 1.2 Fingerprinting of bitumen

Quantification of the eight fractions allows differentiation of materials as shown in Figure 3. This is useful for fingerprinting and discriminating different bitumen sources (Figure 4). Results can be treated with chemometric software to predict various physical properties of bitumen [2, 3]. For instance it is possible to predict the Glover-Rowe (G-R) parameter for several different asphalts from this data. G-R has been proposed as a rheological surrogate for binder strain of unmodified binders that is sensitive to binder aging and highly driven by the shear modulus (stiffness) [4, 5]. Plotted on Black Space diagrams G-R, a point parameter, can be adjusted as a function of test temperature, frequency or even failure limits against climate specifications. G-R is a function of binder shear modulus ( $G^*$ ) and phase angle ( $\delta$ ) at a given frequency  $\omega$ , as presented in equation (1). Note: at a constant frequency, G-R is simplified to be a function of only  $G^*$  and  $\delta$ .

$$G-R = (G^* \cdot \cos^2 \delta / \sin \delta) \cdot \omega \quad (1)$$

Figure 5 shows that G-R is related to bitumen aromaticity as it is influenced by the three aromatics fractions and the toluene-soluble asphaltenes. Aromatics 1 and 2 have a negative correlation on G-R as they contain aliphatic side chains and naphthenic structures leading to binder softening (lower modulus), while Aromatics 3 and Toluene

asphaltenes have a positive correlation as they are highly aromatic containing less aliphatic chains, and therefore leading to hardening (higher modulus).

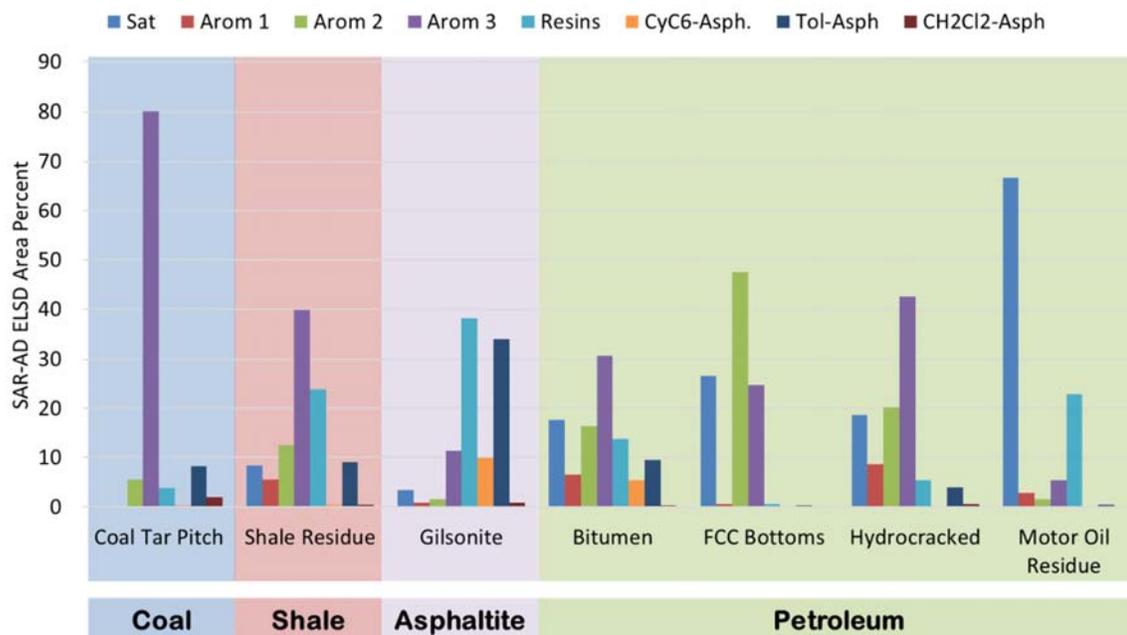


Figure 3: Profiles for some naturally occurring materials and refined materials (FCC is fluidized catalytic cracking).

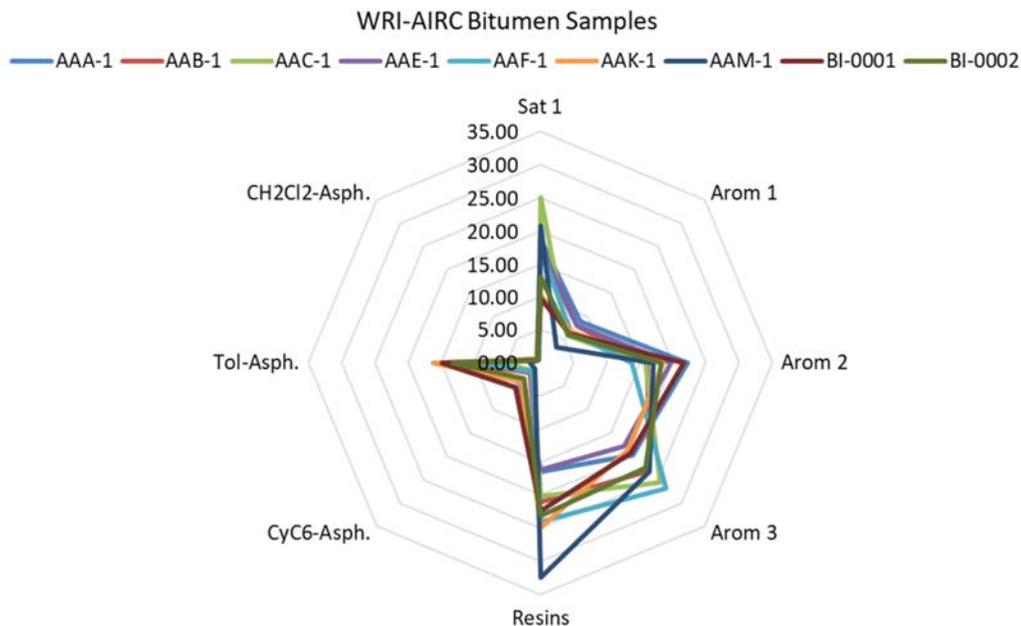


Figure 4: Radar plots for bitumen samples.

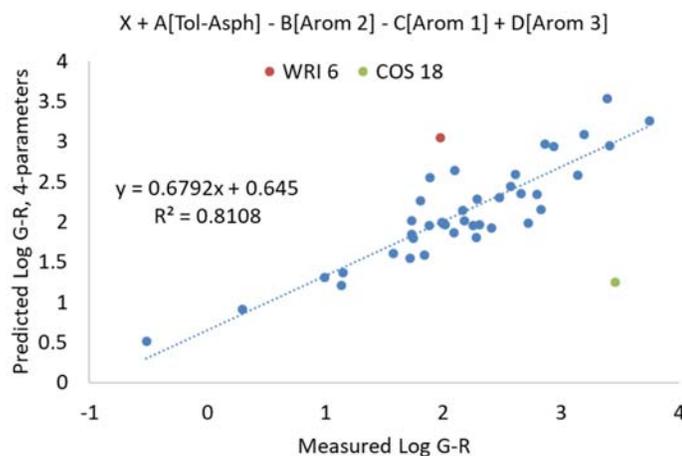


Figure 5: Correlation between the measured and predicted Glover-Row parameters.

### 1.3 Thermal conversion: visbreaking, hydrocracking, catalytic cracking

The AD was initially developed under U.S. Department of Energy funding to quantify and monitor pyrolysis and coking onsets of heavy oils and bitumen. It was observed that as bitumen undergoes pyrolysis (thermal bond breaking/visbreaking) the free solvent volume Cyclohexane asphaltenes decreased while the polar-pre-coke Dichloromethane asphaltenes increased. By taking a ratio of these two, a coking index was developed which is very sensitive to the pyrolysis history [6]. For most bitumen the coking index is between 3 and 16. For visbroken and hydrocracked materials the coking index fall below 3 and is significantly lower depending upon the severity of the conversion. Figure 6 shows some trends in upgraded bitumen materials.

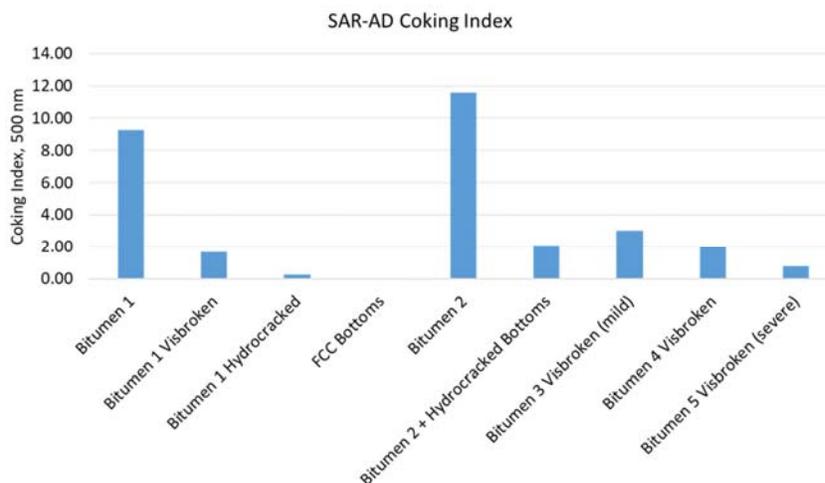


Figure 6: Coking index for bitumen and bitumen processed by visbreaking at different severities, bitumen after hydrocracking, and blends of bitumen.

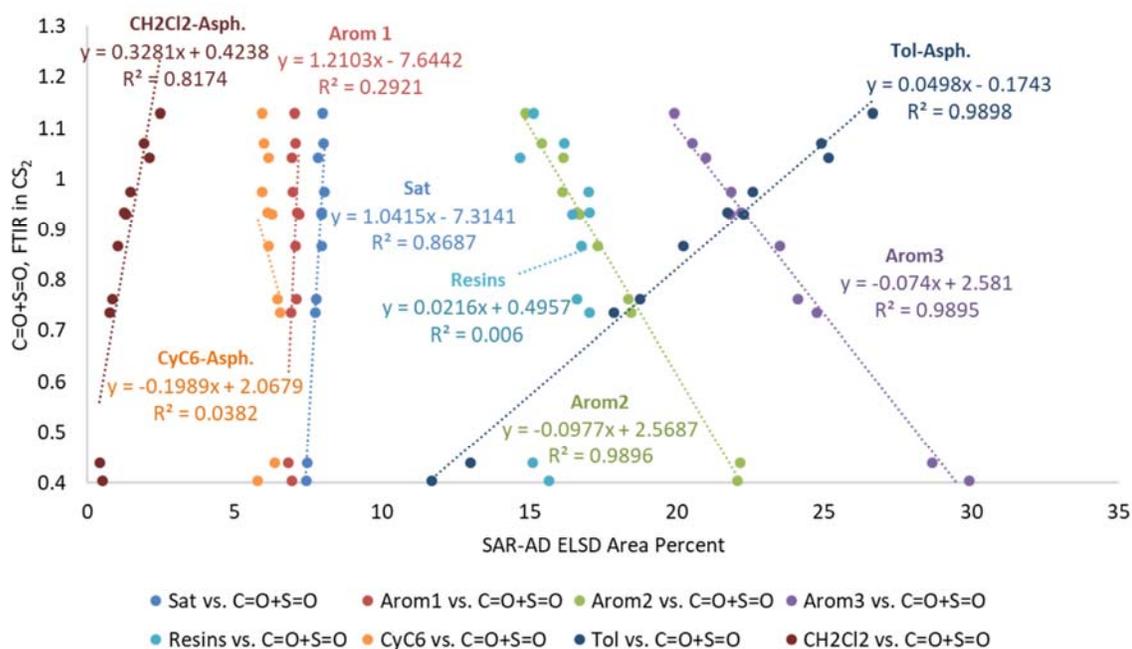
The ability to determine if bitumen has been thermally cracked is important as this process removes aliphatic side chains from aromatic molecules of the resins and asphaltenes which lead to poor relaxation properties in bitumen. This has been observed with several visbroken samples that give  $\Delta T_c$  (Superpave  $T_{critical}$  Stiffness- $T_{critical}$  m-value, from BBR measurement) values that are often less than  $-5$  °C and as low as  $-20$  °C or lower. This indicates that these materials may be highly prone to cracking in the field [7]. Generally these materials are not used for paving (especially the top lift) and are usually used as marine fuel oil. However, with the tightening sulphur restrictions for IMO 2020 regulations [8]—and the fact that partial upgrading is becoming more widely practiced (especially in countries like Canada)—these materials may become more evident in bitumen streams. The Separation is also able to show changes which occur during air rectification, which is also important as this process increases the aromaticity of bitumen. However, with the correct formulation, negative effects on bitumen relaxation and cracking properties

can be mitigated while taking advantage of the improved stiffness and upper temperature properties afforded by these materials.

#### 1.4 Oxidation

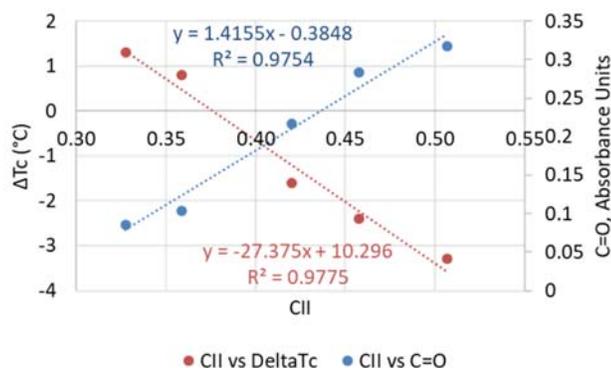
Even well-constructed roads, paved with high quality bitumen, will eventually deteriorate with time due to oxidative aging. Long-term oxidative aging is the chronic “Achilles Heel” for most bitumen: as oxygen diffuses into the bitumen it reacts to produce more polar species while depleting less polar material reducing relaxation properties and causing other secondary problems. For this reason it is important to be able to predict how different bitumens will oxidize in the field and if those levels of oxidation will result in reduced mechanical properties resulting in damage. Some bitumen is significantly more tolerant of oxygen uptake than other bitumen before significant restructuring, stiffening and incompatibility resulting in damage.

Oxidation in bitumen is a complex process where aromatics are consumed to produce resins and eventually asphaltenes. The net change is a decrease in aromatics and an increase in asphaltenes, while resins are a transitory fraction which may go up and down depending upon the original aging characteristics of the bitumen and the severity of oxidation. Changes in bitumen composition upon oxidation are tracked by the Separation [9]. Figure 7 shows how these fractions change for a single bitumen after aging by RTFOT and PAV under several different aging conditions relative to the major carbonyl (C=O) and sulfoxide (S=O) oxidation species from FTIR. From the plot, Aromatics 2 and Aromatics 3 are consumed as these are the most sensitive to oxidation, with Aromatics 3 undergoing oxidation at a slightly higher rate. Toluene asphaltenes also increase the most with oxidation, whereas Dichloromethane asphaltenes increase much slower. There is a small change in the Saturates and Aromatics 1 and no clear trend with the Cyclohexane asphaltenes and Resins. This last point shows that the Resins and Cyclohexane asphaltenes are probably closely related and are both transitory species in the oxidation pathway where they are being produced as oxidation products and also reacting further to produce Toluene and eventually Dichloromethane asphaltenes. These changes have also been observed on bitumens extracted from field cores for different field sites and following the oxidation evolution for more than a decade.



**Figure 7: Changes in fractions using the ELSD relative to oxidation species determined by FTIR.**

Due to the sensitivity in the changes of the different fractions, various aging indices have been developed with traditional metrics such as the colloidal instability index ( $CII = (\text{saturates} + \text{asphaltenes}) / (\text{aromatics} + \text{resins})$ ). The CII can also be used to gather insight into phenomena such as cracking as it has shown good trends with  $\Delta T_c$ . Figure 8 shows a comparison of the Separation CII to the increase of carbonyl species and decrease in  $\Delta T_c$  with increased severity of oxidation.



**Figure 8: Changes in CII with carbonyl and  $\Delta T_c$  with aging severity of bitumen.**

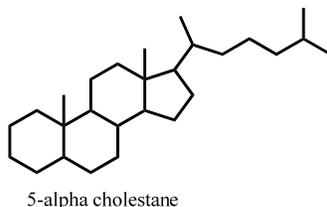
### 1.5 Additives

In efforts to improve the durability, performance and recyclability new additives are being developed for the paving industry. The Separation can discriminate between different additives. Rejuvenator additives that are used to soften bitumen to improve recyclability, typically report to the Saturates, Aromatics or Resins. The fraction(s) to which the additives report can have additional consequences in the overall compatibility of the recycled blends. Polymeric additives can also be detected and quantified such as SBS, which reports to the Cyclohexane asphaltenes.

### 1.6 Model compound study

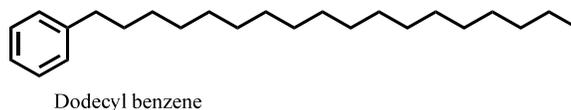
In an effort to better chemically understand the fractions, an extensive study was conducted with model compounds to understand the important molecular features that are responsible for causing molecules to report to the different fractions.

Linear and branched alkanes report to Saturates. It was also determined that highly naphthenic (saturated cyclic molecules), such as 5- $\alpha$  cholestane (Figure 9), also report to Saturates.



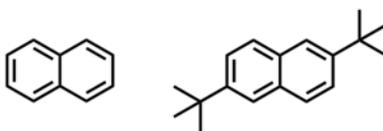
**Figure 9: Molecular structure of 5- $\alpha$  cholestane.**

Figure 1 shows that Saturates and Aromatics 1 are closely related: both are eluted and separated by the same mobile phase from silica gel. The difference is that molecules in Aromatics 1 contain one aromatic ring, as confirmed with the model compound dodecyl benzene (Figure 10). However molecules containing a single aromatic ring must have a high enough molecular weight to prevent them from being distilled during refining, meaning such molecules must have a very high degree of substitution of alkyl and naphthenic rings around the aromatic ring. This substitution causes steric hindrance preventing interaction with the stationary phase, causing Aromatics 1 to behave chromatographically similar to Saturates.



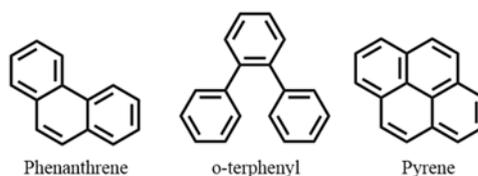
**Figure 10: Molecular structure of dodecyl benzene.**

Steric hindrance for highly substituted aromatics was confirmed by analysis of naphthalene and di-tert-butyl-naphthalene (Figure 11 left and right, respectively). Naphthalene reports exclusively to the Aromatics 2, whereas tert-butyl substitution prevents from complete adsorption of the naphthalene core on silica gel and about 40% of the compound elutes with Aromatics 1.



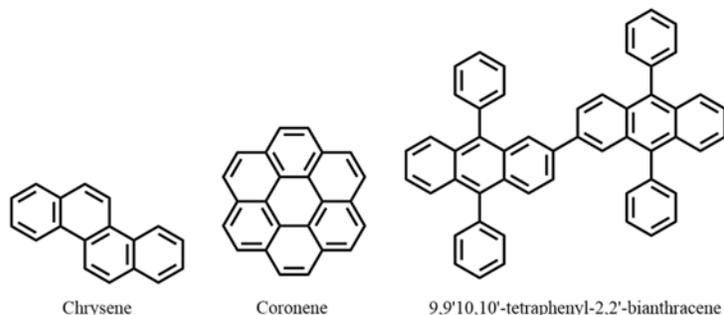
**Figure 11: Molecular structures reporting to the Aromatics 1 and Aromatics 2.**

Figure 12 shows other compounds that report to the Aromatics 2 consist of fused two-ring and three-ring aromatics (left), three-ring aromatics with carbon-carbon bonds between the aryl groups (centre), four-ring aromatic systems with non-fused rings, and the four-ring pericondensed aromatic pyrene (right). Molecules with two or three aromatic rings with thiophene, cyclic sulphides and cyclic ethers also report to Aromatics 2. This fraction is important because it contains molecules which are highly sensitive to oxidation and is the generally the second most abundant in bitumen.



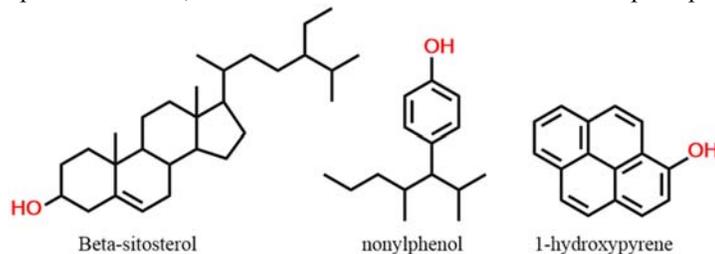
**Figure 12: Other complex molecular structures reporting to Aromatics 2.**

Aromatics 3 which is usually the most abundant bitumen fraction, contains molecules with four or more rings. These can be catacondensed fused ring systems like chrysene, pericondensed fused seven-ring systems like coronene, or other combinations of multiple fused ring molecules (Figure 13). This fraction is one with the highest aromaticity within bitumen, generally low in heteroatoms and highly oxidation sensitive. Aromatic molecules with low polarity heteroatoms (carbazoles) can report to this fraction, including molecules that would normally report to Aromatics 2 in the absence of their weakly polar functional groups.



**Figure 13: Molecular structures which report to Aromatics 3.**

Molecules reporting to Resins contain polar heteroatoms (phenolic, pyridinic, some ethers, ester and carboxylic). Many of them would normally report to Aromatics or Saturates in the absence of polar functional groups. The fact that this fraction has a strong brown colour (absorbing light at 500 nm) indicates that the majority of molecules within this fraction contain aromatic chromophores. Figure 14 shows representative model compounds reporting to Resins that would otherwise report to Saturates, Aromatics 1 and Aromatics 2 without their polar phenolic groups present.



**Figure 14: Molecular structure for molecules reporting to the Resins.**

## 2. 2<sup>nd</sup> GENERATION DEVELOPMENT

Although the first generation Separation is a powerful tool to discern many bitumen properties, it has some limitations to distinguish certain properties. Additional capabilities are being added to provide a next-generation instrument that that will bring better correlations between the fractions and the mechanical properties and performance of bitumen.

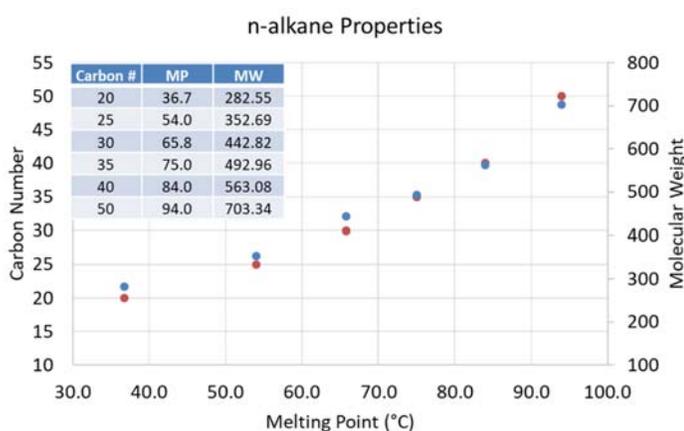
At the molecular level, some important features can drive viscosity/stiffness. To provide a more holistic understanding of how the various fractions influence the bitumen viscosity additional information are necessary such as:

- 1) Molecular weight
- 2) Aromaticity, especially for heavier fractions like Aromatics 3, Resins and Asphaltenes
- 3) Polarity and hydrogen bonding of the functional groups in Resins and Asphaltenes
- 4) Molecule geometry (linear, branched, cyclic)

Efforts to address items 1-3 are generically described below.

### 2.1 Separation + SEC

Molecular weight (MW) can be measured using size exclusion chromatography (SEC). SEC has long been practiced to understand some parameters about the bitumen MW. Figure 15 shows how it can provide simple insight into the stiffness of the SAR fractions by looking solely at n-alkanes as one narrow class of compounds present in the Saturates.



**Figure 15: Relationships of n-alkanes for chain length, molecular weight and melting point.**

Traditionally, bitumen SEC has been complicated by overlap between maltenes and asphaltenes. Analysis of the asphaltenes is also more complicated due to apparent high MW bias from the strong molecular associations. Although these associations are important, and can be used as stiffness indicators of the whole asphalt, they are difficult to interpret as true MW assessment. To overcome these issues, the Separation can be used to separate asphaltenes from maltenes which can then be analysed by SEC. Figure 16 depicts comparative SEC profiles of two SHRP bitumens AAM-1 (high MW) relative to AAG-1 (low MW). Hence, this separation and analysis allows to diagnose visbroken residues, air rectified bitumen, identify polymers such those in REOB (re-refined engine oil bottom) and also show the effect of PPA (polyphosphoric acid) [10]. Future developments will be providing SEC of select fractions.

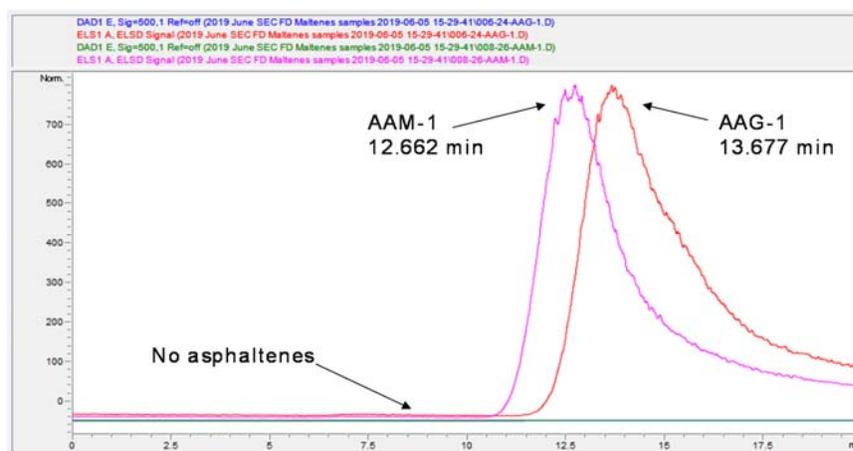


Figure 16: SEC of maltenes of AAG-1 and AAM-1.

Current developments, not presented here, involve the implementation of a calibration technique allowing to measure more realistic molecular weight of bitumen and fractions, not involving polystyrene standards.

## 2.2 Separation + FS

From the model compound study, Aromatics 3 can contain molecules with aromatic cores with four or more fused rings. Knowing the size range of the aromatic cores would help to assess the impact on stiffness of these fractions and the whole bitumen. Fluorescence spectroscopy (FS) can be used to elucidate size and structure of fused aromatic rings. Table 1 shows a simplistic relationship between the number of fused aromatic rings and melting point, with melting point increasing significantly with the ring number for pericondensed aromatic molecules.

Table 1. Some relationships between the number of aromatic cores, shape and melting point.

# Fused Rings	Molecule	MW	Melting Point, °C	Shape (linear, cata, peri)
2	naphthalene	128.17	80	linear/peri
3	phenanthrene	178.23	101	cata/peri
	anthracene	178.23	216	linear
4	pyrene	202.25	145	peri
	chrysene	228.29	254	cata
	tetracene	228.29	357	linear
	triphenylene	228.29	438	cata
5	benzo-a-pyrene	252.32	179	peri
	dibenzo-a,h-anthracene	278.35	262	cata
	perylene	252.32	276	peri/cata
	pentacene	278.35	>300	linear

Assuming that the fused aromatic ring structures are mostly pericondensed, FS can provide some insight to the structure of the fused ring systems as a more red-shifted maximum in the emission spectra, or greater Stokes Shift, will indicate a greater number of fused rings. These shifts should represent how many fused rings are present and provide meaningful comparisons between the same fractions between different bitumens.

Figure 17 data explains some additional behaviour of AAM-1 compared to AAD-1. From SHRP data AAM-1 has little n-heptane asphaltenes (4.0%) but significantly higher average MW (1030 Daltons) compared to AAD-1 which has a high amount of asphaltenes (20.5%) and a much lower MW (700 Daltons). Since AAM-1 has a PG 66.5 and AAD-1 61.4, the higher stiffness of AAM-1 is clearly governed by its MW. AAM-1 is also known for containing significantly higher MW waxes. Applying FS shows that the number of aromatic cores in Aromatics 2, Aromatics 3 and Resins of AAM-1 are greater than AAD-1. This is inferred by comparing the red-shift in the maximum of the emission spectra from these fractions.

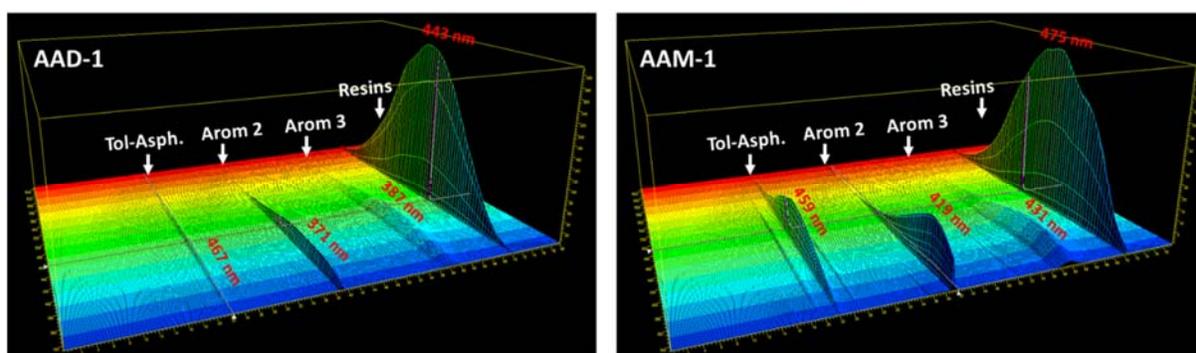


Figure 17: FS of the fractions for AAD-1 and AAM-1 with the maximum of the emission spectra indicated in red.

### 2.3 Separation + FTIR

Of the fractions, Resins and Asphaltenes contain the largest amount of heteroatoms and also the most polar heteroatoms. These heteroatoms are important to how these molecules provide additional structuring to the bitumen beyond the properties (MW, aromaticity, etc.) of the individual molecules. This structuring can be due to hydrogen-bonding (H-bonding), acid-base or dipole-dipole interactions. This structuring can lead to oligomerization if molecules containing two or more complimentary functional groups associate, and influence the core-shell colloidal stability of the asphaltenes and resins for example. One way to probe the structuring potential of the resins and asphaltenes is to discriminate and quantify between the types of functional groups present, using FTIR spectroscopy. Figure 18 shows FTIR spectra in the H-bonding region for two bitumens before and after 2PAV aging, differentiating unaged and aged bitumens H-bonds.

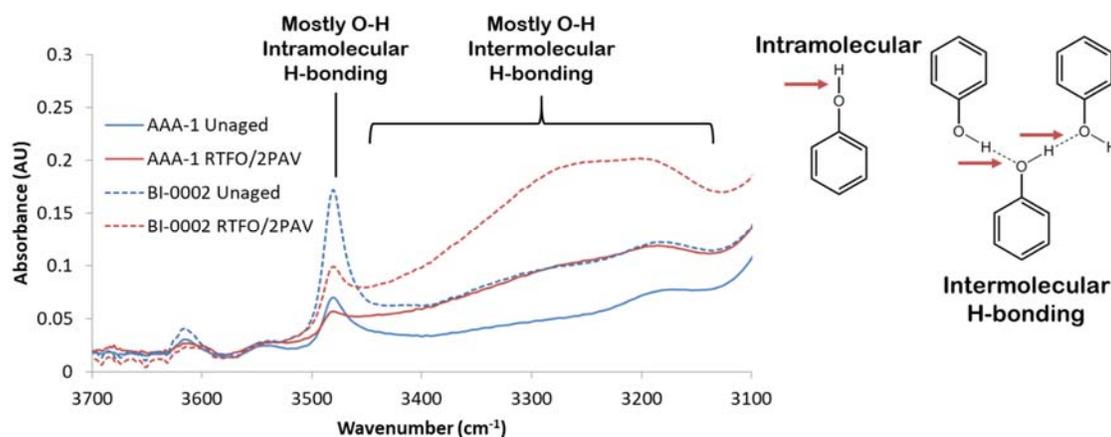


Figure 18: The left shows FTIR spectra differences in the intra and intermolecular H-bonding between two bitumens before and after aging. The right illustrates the difference between intra and intermolecular H-bonding for phenol.

Several additional chemical features of fractions include aromaticity, branching, aromatic ring substitution patterns, heteroatom functional groups and amount of consecutive methylene units greater than 4 units. These features can help understand how they influence bitumen physical properties and they interact with additives or polymers and influence oxidation. Important FTIR spectral features are shown in Figure 19 [11].

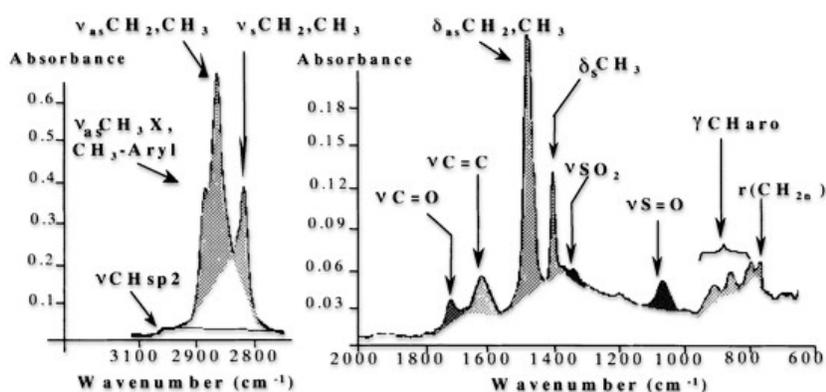


Figure 19: FTIR spectral regions of interest to bitumen with assignments [11].

It is widely accepted that as bitumen oxidizes that the net effect is that most of the oxygen ends up in the asphaltenes. However, as demonstrated earlier, the resins is a transitory fraction where some aromatics are oxidized to form resins before becoming asphaltenes. Figure 20 shows that after aging there are a significant amount of sulfoxides present in Resins as well as Toluene asphaltenes.

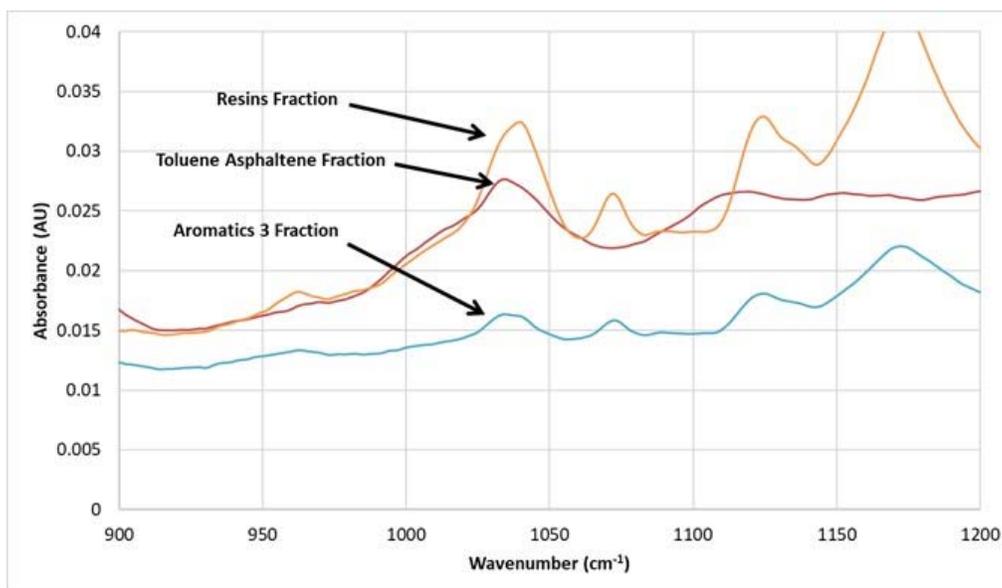


Figure 20: FTIR spectra of fractions after aging showing the sulfoxide region.

## CONCLUSIONS

The SAR-AD technique combines chromatography and solubility separations to fractionate bituminous materials. Data from this hybrid separation method is useful for fingerprinting hydrocarbon materials, predicting physical properties of bitumen, diagnosing visbroken/upgraded bitumen, diagnosing air blowing, tracking oxidation, polymer compatibility and analysing additives. An extensive model compound analysis study has allowed to define more precisely what molecular structure report to each individual maltene fractions.

As the Separation database continues to expand some limitations have been uncovered. Namely, there is a fairly small percentage of bitumens with the same Separation profile that have different mechanical properties, or compatibilities with polymers for example. To reduce these limitations additional information is needed on the fractions, which has led to ongoing development of the next generation analysis.

The next generation provides multidimensional characterization of the fractions, particularly regarding their molecular associations, aromatic structures and sizes, and chemical functionalities by SEC, FS and FTIR. Preliminary

results show that these capabilities are bringing significantly more insight into bitumen mechanical properties, effects of additives, and effects of bitumen processing conditions.

This work is ultimately dedicated to help suppliers and users to properly design bitumen materials in a changing binder supply and production context, influenced by a variety of factors such as the IMO specification for bunker fuels [8].

## ACKNOWLEDGEMENTS

Funding for the model compound study was provided by the University Of Wyoming School Of Energy Resources. The authors are grateful to the funding, samples and discussions provided by the AIRC and/or HORC partners (BRRC, Eiffage, Eurovia, ExxonMobil, FHWA, Husky Energy, IFSTTAR, Petrobras, Puma Bitumen, Repsol, RoadMat, Shell, Surfax, and Total). They also acknowledge Nick Bolton for his significant contribution on 2nd generation instrument experiments, and other WRI employees on the characterization of the huge sample base.

## REFERENCES

- [1] Boysen, R.B.; Schabron, J.F.; "The Automated Asphaltene Determinator Coupled with Saturates, Aromatics, and Resins Separation for Petroleum Residua Characterization", *Energy and Fuels*, 27, 2013, 4654-4661, 10.1021/ef400952b.
- [2] Delfosse, F.; Drouadaine, I.; Faucon-Dumont, S.; Largeaud, S.; Eckmann, B.; Planche, J.P.; Turner, F.; Glaser, R. "Impact of the Bitumen Quality on the Asphalt Mixes Performance", 6th E&E Congress, Prague, Czech Republic, 2016.
- [3] Glaser, R.; Planche, J.P.; Turner, F.; Boysen, R.; Schabron, J. F.; Delfosse, F.; Drouadaine, I.; Faucon-Dumont, S.; Largeaud, S.; Eckmann, B. "Relationship between Solubility and Chromatographically Defined Bitumen Fractions and Physical Properties", 6th E&E Congress, Prague, Czech Republic, 2016.
- [4] Glover, C. J., R. R. Davison, C. H. Domke, Y. Ruan, P. Juristyarini, D. B. Knorr, and S. H. Jung. (2005) "Development of a new method from assessing asphalt binder durability with field validation", TTI Report FHWA/TX 05-1872-2, 2005.
- [5] Rowe, G. (2011) "Prepared Discussion presented in response to M. Anderson, et.al", *Journal of AAPT*, V 80, 2011.
- [6] Schabron, J.F.; Rovani, J.F., Sanderson, M., "Asphaltene Determinator Method for Automated On-Column Precipitation and Redissolution of Pericondensed Aromatic Asphaltene Components", *Energy and Fuels*, 24, 2010, 5984-5996. <https://doi.org/10.1021/ef100822f>.
- [7] Anderson, R. M., King, G. N., Hanson, D. I., Blankenship, P. B. "Evaluation of the Relationship between Asphalt Binder Properties and Non-Load Related Cracking", *Journal of the AAPT*, 80, 2011, pp. 615-649
- [8] International Maritime Organization (IMO) (2016) "IMO sets 2020 date for ships to comply with low sulphur fuel oil requirement", IMO briefing, <http://www.imo.org/en/mediacentre/pressbriefings/pages/mepc-70-2020sulphur.aspx>
- [9] Automated High-Performance Liquid Chromatography Saturate, Aromatic, Resin, and Asphaltene Separation, FHWA Publication No.: FHWA-HRT-15-055, 2016.
- [10] Adams, J.J. ; Rovani, J.F. ; et. al. "SAR-AD Innovations and Next-Gen Developments", 55th Petersen Asphalt Research Conference, 2018, Laramie, WY, USA.
- [11] Lamontagne, J.; Dumas, P. et. al., "Comparison by Fourier transform infrared spectroscopy of different ageing techniques: application to road bitumens", *Fuel*, 80, 2001, 483-488. 10.1016/S0016-2361(00)00121-6.