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The role of sulfur in bitumen properties

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Contents

1 Introduction

In recent years, the Dutch market has experienced quality issues and inconsistencies in bitumen supply which have raised concerns in performance, workability, health and safety aspects in the asphalt sector. Uncertainties are broadly related to cost, availability and properties of bitumen. These are believed to be caused due to the closure of bitumen production in refineries around this area, and non-refiners entering in the supply chain. Moreover due to the change in fuel demand, refineries are going through transitions with major upgrading in their processing technologies which led to more variation in production properties and as a result: varying composition of bitumen products.

One of the discussed topics in the sector is the legislation introduced by International Maritime Organization (IMO) which has been implemented since 1st of January 2020 [1, 2, 3]. IMO 2020 act is to reduce global sulfur oxides (SO_x) emissions from heavy fuel oil used in the ships and hence the sulfur content in the marine fuel is reduced from 3.5% to 0.50% m/m (mass by mass). It has impacted the selection of crude oil sources, the refining processes as well as the whole value chain of the bitumen market: from the product grades to the price.

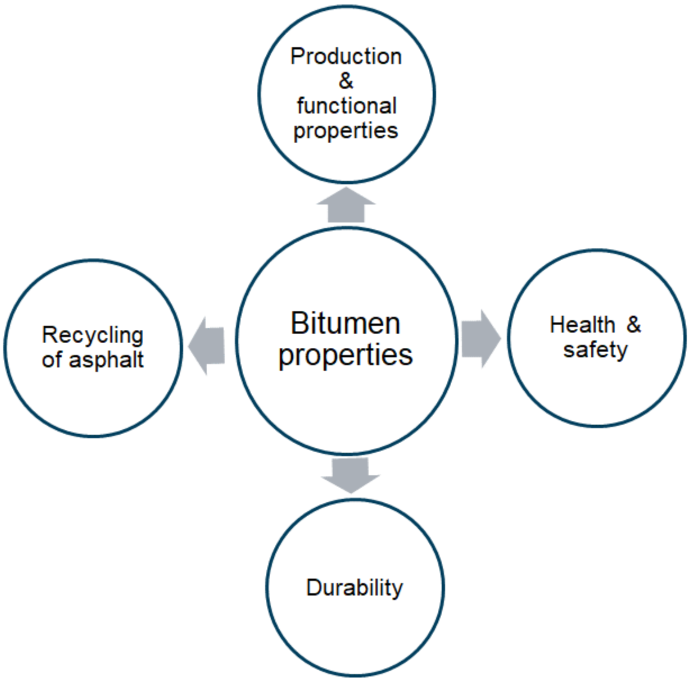


Figure 1: Impact of bitumen properties into different aspects of the value chain.

Bitumen property variation influences primarily, but is not limited to the following aspects of applications and performance (Figure 1):

- Production and operational properties during application.
- Health, safety and environmental aspects in the value chain.
- Properties in relation to durability and
- Reclaimed asphalt binder properties after end of service life and its suitability for asphalt recycling.

Bitumen is a complex mixture of hydrocarbons, where next to hydrogen and carbon the molecules contain small quantities of sulfur, nitrogen, oxygen (i.e. commonly termed as heteroatoms) and trace metals. Sulfur is known to be the most abundant among the other two heteroatoms, oxygen and nitrogen, naturally present in bitumen. It introduces polarity along with nitrogen and oxygen and regulates molecular interaction in bitumen [4,5,6]. One of the key concerns that rose from the current situation is whether the sulfur content in bitumen can potentially change in future bitumen products and the consequence on sulfur content on bitumen properties. Hence, compositional information is instructive to have better insights on performance properties of bitumen and how bitumen can differ due to different sources and production processes. This was the motivation to write a literature review focused on the role of sulfur in chemical composition of bitumen and to elucidate the relationship between the composition of bitumen and performance properties. This review is a part of Task-1 as proposed in the plan of approach of the project- “Characterization and Evaluation of Asphalt Binder Properties” within the Knowledge-based Pavement Engineering (KPE) program.

2 Objectives of the review

The objective of the review is to summarize the state of the art knowledge available on the influence of sulfur in bitumen properties and to present the need for attention in relation to continually changing properties of bitumen due to variation in crude oil sources and upgrading of the production processes.

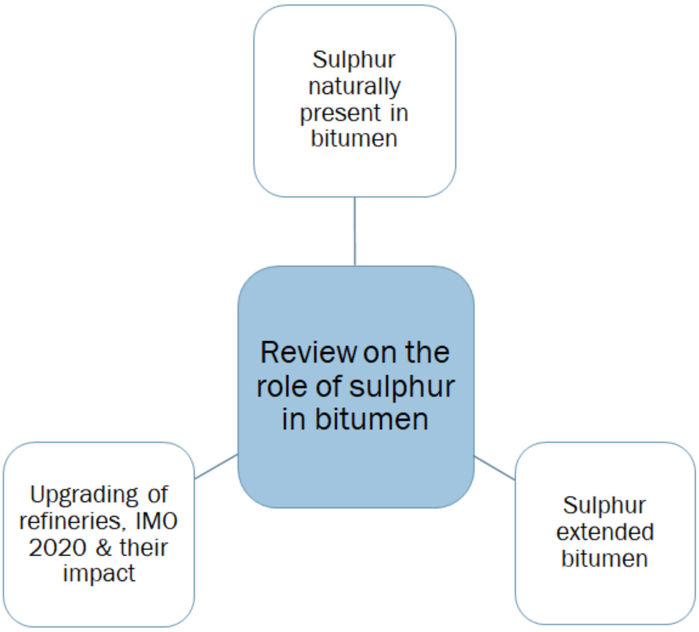


Figure-2: Content of the review.

The review covers three aspects of the role of sulfur in bitumen properties as presented in Figure-2.

- Sulfur as naturally present in bitumen and its role in structure and properties.
- The properties and contributions of Sulfur modified or extended bitumen.
- Upgrading of the refineries, IMO 2020 and their impact on the content of sulfur and properties of bitumen.

3 Sulfur as naturally present in bitumen

3.1 Composition of bitumen:

Bitumen is mostly obtained as a heavy residue from distillation of crude oil in petroleum refining. At the molecular level, bitumen is a mixture of thousands of dissimilar high boiling point hydrocarbons: aliphatic, aromatic and a mixture of both. Although bitumen molecules are composed predominantly of carbon and hydrogen, they commonly contain so called heteroatoms like nitrogen (≤2%), oxygen (≤2%), sulfur (≤6%), and trace amounts of metals, mainly vanadium and nickel [5, 6, 7, 8]. Aliphatics in bitumen are saturated long chain, branched paraffins, polycyclic structures, or unsaturated olefins. The hydrocarbon components fall into other classes like Naphthenes that are saturated hydrocarbons with one or more rings. These hydrocarbons may have one or more paraffinic side chains. Aromatics are hydrocarbons with one or more aromatic nuclei; these hydrocarbons may be connected to naphthenic rings and/or paraffinic side chains. The core structures of the aromatics are different numbers of aromatic fused rings (i.e. polyaromatic structure). Other classes of molecules are found as combinations of aliphatic and aromatic structures with aliphatic side chains, with possible substitutions of heteroatoms and trace metals. Bitumen processed from certain crude oil sources may contain 2 to 5 w% of wax [5, 6]. Waxes in bitumen are found as paraffinic wax, which consists of n-alkanes with few or no branches, and microcrystalline wax that contains mainly naphthenes (saturated rings) and iso-paraffines.

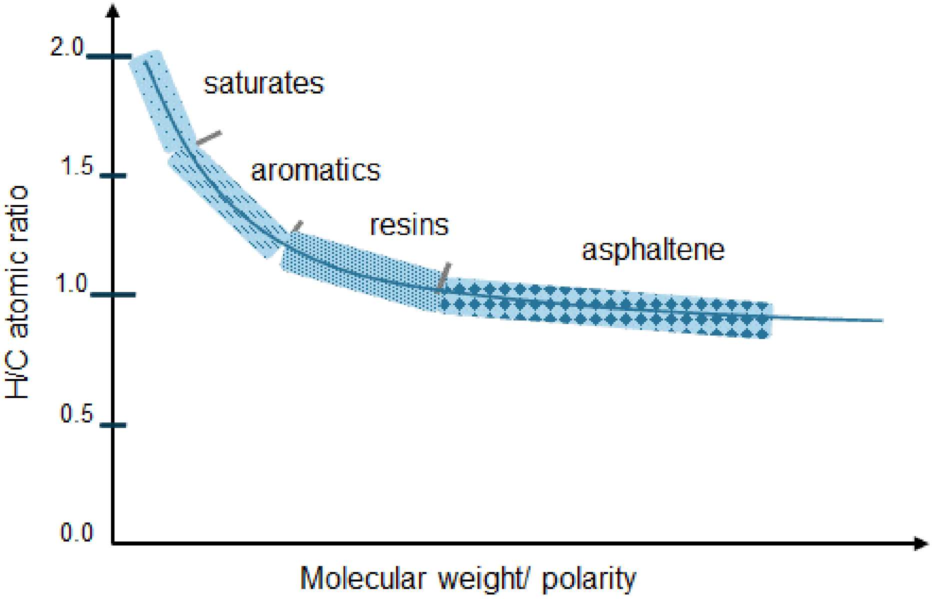


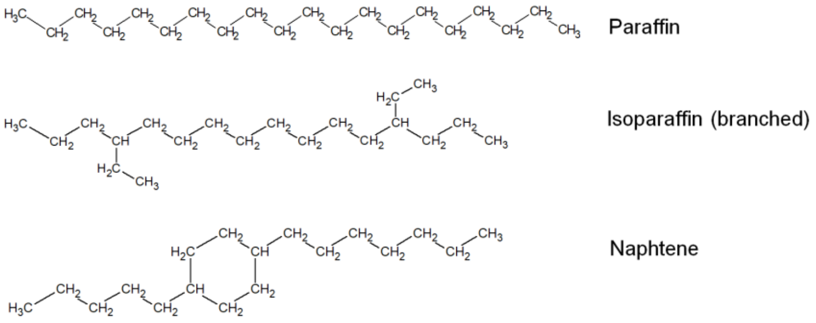
Figure 3: Schematic presentation of hydrogen to carbon atomic ratio of the SARA fractions of molecular classes of bitumen.

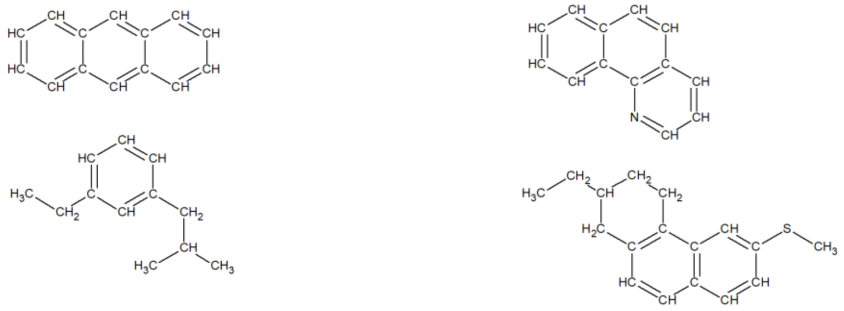
3.1.1 *SARA molecular fractions:*

To simplify the diversity of the chemical nature of bitumen, researchers took pragmatic approaches to separate bitumen into various chemical fractions. Different separation techniques were adapted on the basis of molecular size, reactivity, solubility and polarity [5, 6, 7]. One of the most accepted separation techniques on the basis of polarity is SARA analysis. The fractions are commonly known as:

saturates, aromatics, resins and asphaltenes (SARA) as shown in Figure 3. The molecular weight and the aromaticity of the fractions increase as saturates → aromatics → resins → asphaltenes [8, 9, 10, 11]. SARA fractionation can also be explained by hydrogen to carbon atomic ratio, that decreases with increasing molecular weight. Hence the H/C atomic ratio gradually decreases from saturates to asphaltenes [8, 9].

(a) Saturates




(b) Aromatics

(c) Resins

(d) Asphaltenes

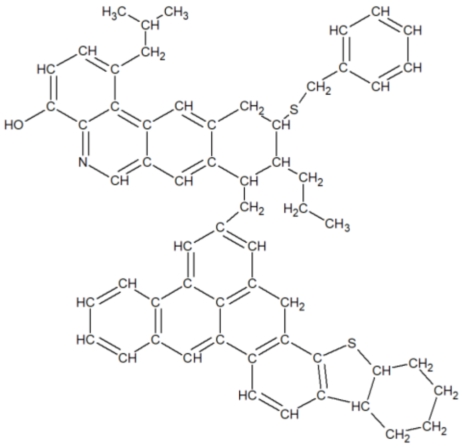


Figure 4: Representative molecular structures of bitumen SARA fractions. (after [9])

SARA fractions are experimental boundaries of a continuous range of molecules; hence molecular properties can vary within a fraction. There is small difference in polarity between the fractions. The selection of solvents defines the boundary of the fraction and if shifted then a portion of molecules will become a part of the next fraction [6]. The first three fractions in SARA are typically known as 'maltenes' which are soluble in n-alkanes. Whereas, asphaltenes are insoluble in n-alkanes and different types of asphaltene molecules precipitate according to the choice of n-alkane. High molecular weight n-alkanes, containing more than 40 carbon atoms co-precipitate with asphaltenes [12].

Saturates are mainly paraffins, naphthenes and a mixture of the two, Figure 4(a). The aromatic fraction is a mixture of paraffins, naphthenes and aromatics with sulfur containing compounds, Figure 4(b). Resins contain similar molecular classes as the aromatics, with multi-ring structures and heteroatoms (N, O, S), Figure 4(c). The asphaltene fraction consists of paraffins, naphthenes and aromatics composed into polycyclic structures containing heteroatoms [13] Figure 4(d).

3.2 Elemental composition

Extensive studies on composition and its influence on chemical and physical properties of bitumen are performed in the Binder Characterization and Evaluation project within the Strategic Highway Research Program (SHRP) in US [14]. The study is reported in SHRP- 368 Volume 2 and primarily included a selection of eight SHRP bitumens for detailed compositional analyses in the first phase of the research program. In relation to the influence of sulfur in bitumen properties, four bitumens are selected from the SHRP program on the basis of different sulfur content: AAD-1, AAK-1, AAM-1 and AAG-1 and have been presented in detail in the following sections. In this selection, AAD-1 and AAK-1 are higher in sulfur content whereas AAM-1 and AAG-1 are low in sulfur.

3.2.1 Carbon and hydrogen content

The atomic hydrogen-to-carbon (H/C) ratio is commonly used in the petroleum industry to assess fuels and their different fractions. A high H/C value in fuels indicates that they are hydrogen rich and are aliphatic in nature. In saturate fractions, H/C is nearly 2, whereas coals have H/C ratio close to unity. The lower the H/C value of a fraction, the more richer they are in carbon and this indicates relative high aromaticity of the material. As presented earlier in Figure 3, the H/C atomic ratio decreases from saturates to the asphaltene fraction in bitumen.

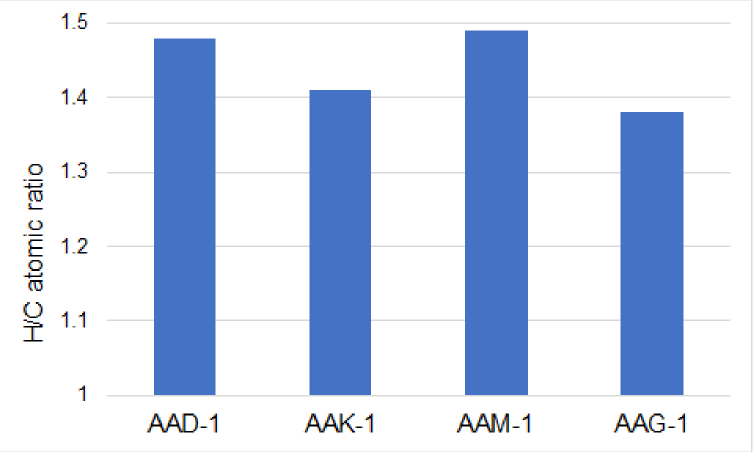


Figure 5: H/C atomic ratio of four core bitumen from SHRP research [14].

The H/C atomic ratios of the four core bitumens from SHRP research are presented in Figure 5. Usually carbon content of bitumen and related fractions varies over a narrow range (i.e. 80–85 wt.%), whereas hydrogen content can be 12-14 wt.% in lighter distillates and approximately 5 wt.% in heavy residues (i.e. highly viscous bitumen). Hence hydrogen content is more instructive in assessing properties of bitumen [15]. In AAD-1, AAK-1, AAM-1 and AAG-1 bitumens, the H/C ratios vary from 1.38 to 1.49. As the values are not significantly different, it implies that the aromaticities of these bitumen are similar [14].

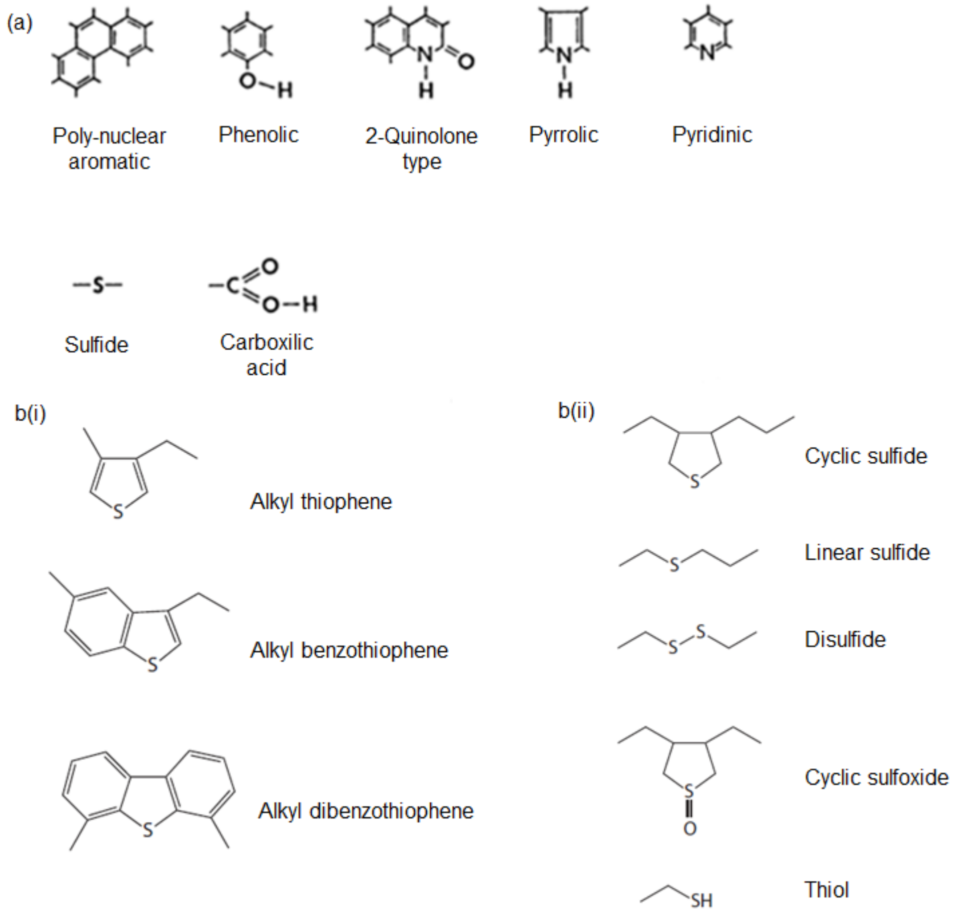


Figure 6: (a) Heteroatoms containing functional groups in bitumen. Sulfur species in bitumen (bi) Thiophenic sulfur (bii) organic sulfides. [after 14, 15]

3.2.2 *Heteroatomic groups*

Sulfur, nitrogen along with oxygen are important components of bitumen, and are commonly known as heteroatoms which facilitate intermolecular interactions in the material. Neat bitumen does not contain sulfur or nitrogen in elemental form.

Heteroatoms containing functional groups as present in neat bitumen are shown in Figure 6a. Sulfur is present in bitumen in the form of sulfides (R-S-R’), thiols (R-SH), and sulfoxides (S=O). Common oxygen containing functional groups are ketones (C=O), phenols (C_6H_5OH), and carboxylic acids (COOH). Nitrogen is found in the form of cyclic conformations such as pyrrolic (C_4H_4NH), pyridinic (C_5H_5N), and 2-quinolone (C_9H_7NO) structures. Among these moieties, some groups result in polar interactions and hydrogen bonding due to their permanent dipoles resulting from inhomogeneous distribution of electrons. The electronegative atoms, nitrogen and oxygen are the main contributors to polarity in the molecular systems [4, 7, 16].

3.2.2.1 *Sulfur*

Sulfur is the most abundant heteroatom in most bitumen. The sulfur content of crude oil varies significantly with source, from about 0.5 to 9 wt.%. Moreover, the concentration may also change due to refining conditions and processes. Sulfur is present in two main forms in bitumen: aromatic rings (Figure 6bi) and organic sulfides (Figure 6bii). The aromatic rings are resistant to conversion by hydrogenation [7, 15, 17]. In neat bitumen sulfur is usually found to be distributed in all component fractions. SARA analyses show that the sulfur concentration in the asphaltene fraction is generally the highest compared to other fractions. However, sulfur species are also found in saturates, resins and aromatics. In general the sulfur concentration increase from saturates → aromatics → resins → asphaltenes.

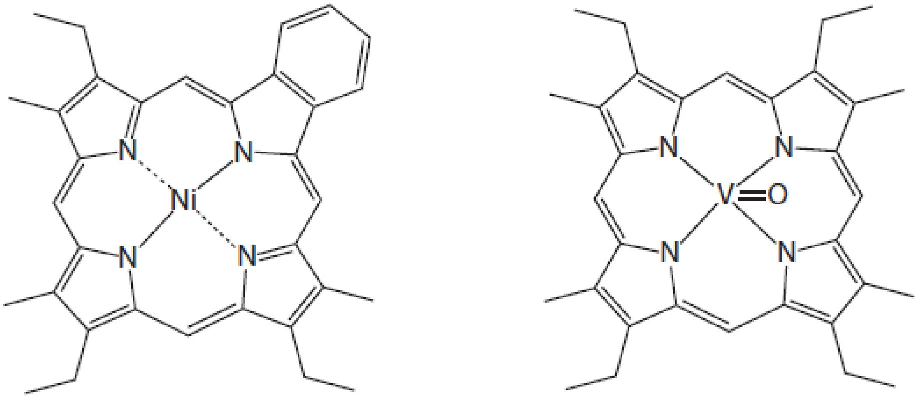


Figure 7: Nickel and Vanadium porphyrin structures in bitumen. [after 15]

3.2.3 *Trace metals*

Vanadium (V), nickel (Ni) and iron (Fe) are trace metals that are intrinsically present in bitumen. Metals are known to be associated with the asphaltene fraction of bitumen in the form of porphyrin-like organometallic complexes in which the metallic cations are bonded to the heteroatoms as seen in Figure 7 [8, 14, 15, 18].

3.2.3.1 *Metalloporphyrins*

The vanadium- and nickel-containing compounds occur mainly as substituted porphyrins as shown in Figure 7. The metal atoms are found to be coordinated with nitrogen in the porphyrin ring structures. The specific backbones for each metal compound are illustrated in Figure 7, where nickel and vanadium atoms are coordinated with four pyrrolic nitrogen, in the porphyrin structure. Another notable finding is the identification of sulfur incorporated into porphyrin structures. Vanadium–sulfur compounds are characterized as thiophenic rings attached to the vanadyl porphyrins [19].

3.2.3.2 *Oxidation characteristics of the metalloporphyrins*

The effect of metalloporphyrins on bitumen oxidation properties were studied by several researchers in the past. The type of metal and its porphyrinic and non-porphyrinic fractions mainly govern the propensity of bitumen to oxidation [8, 11, 14, 18]. Vanadyl porphyrins are found to promote bitumen oxidation, whereas nickel porphyrins show less or no activity in relation to oxidation. However, the correlation of the metal concentration in bitumen and its susceptibility to oxidation is not conclusive. The apparent reason is that the molecular structure in bitumen varies from source to source, introducing different contents and types of oxidizable molecules. The trace elements in bitumen are so-called transition metals which can occur in several oxidation states. For example, vanadium can occur as V^{2+}, V^{3+}, V^{4+} and V^{5+}, which also influences the role of metals in susceptibility to oxidation. Concentrations of trace metals, especially vanadium, is a good indicator for the aging propensity bitumen [11, 14, 18].

3.3 Molecular interactions:

Molecular interaction is the key that drives most of the structuring in bitumen. Interaction establishes the link between the composition to physical property relation. Commonly, molecules composed of carbon and hydrogen tend to associate with one another less strongly than molecules composed of hydrocarbon and heteroatoms such as sulfur, nitrogen and oxygen [14].

The heteroatoms, although being a minor component compared to the hydrocarbon moiety, can vary in concentration and nature over a wide range, depending on the source of the bitumen. Eventually, that makes an impact on the differences in chemical and physical properties among bitumen from different sources.

On the basis of their nature and electronegativity, heteroatoms impart different functionalities and polarity to the molecules. They are incorporated within ring or non-ring components, or in more discrete chemical functional groups attached to these components. The heteroatoms and the aromatic ring systems contribute a considerable polarity or polarizability to the molecules that drives the association forces influencing the physical properties [7, 4, 14].

There are three main types of molecular interactions in bitumen: dispersive, polar and hydrogen bonding. Non-polar hydrocarbon molecules induce temporary dipoles that lead to some weak attractive forces known as London dispersive interactions. Dispersive interaction is important for the physical properties of bitumen and known to determine properties like the boiling point and viscosity [6]. In addition, another kind of dispersive interaction, π-π interactions occurs due to delocalization of π electrons in aromatic molecules. The effect of the interaction is high for larger aromatic systems (i.e. four or more fused rings) and also increases with the number of aromatic rings. The higher boiling point of polyaromatic hydrocarbons compared to same-sized saturated hydrocarbons is the result of such interactions. The presence of substituted heteroatoms (i.e. N, S and O) in the aromatic ring also enhances these interactions [6, 7, 14, 16]. The heteroatom-containing groups are identified as carboxylic acids (COOH), anhydrides (R(CO)O(CO)R’), ketones (C=O), 2-quinolones (C9H7NO), sulfoxides (S=O), pyrrolic (C4H4NH) and phenolic (C6H5OH) types and take part in intermolecular interaction.

Additionally these heteroatoms containing groups contribute to the polarity in bitumen. Heteroatoms induce an inhomogeneous distribution of electrons (i.e. permanent dipoles) and result in some polar interactions and hydrogen bonding. Acidic groups such as carboxylic acids can interact directly with bases such as pyridine groups to form salts. This strong association can drive asphaltene aggregation. Again hydroxyls and carboxylic acids potentially can participate in hydrogen bonding with weak nitrogen bases.

3.4 Bitumen microstructure and phase separation characteristics

The microstructure of bitumen evolves from its chemical composition and intermolecular interaction. Earlier works have shown that there are evident correlations between microstructural properties of bitumens and their relation to crude origin sources, hardness and composition (Figure 8).

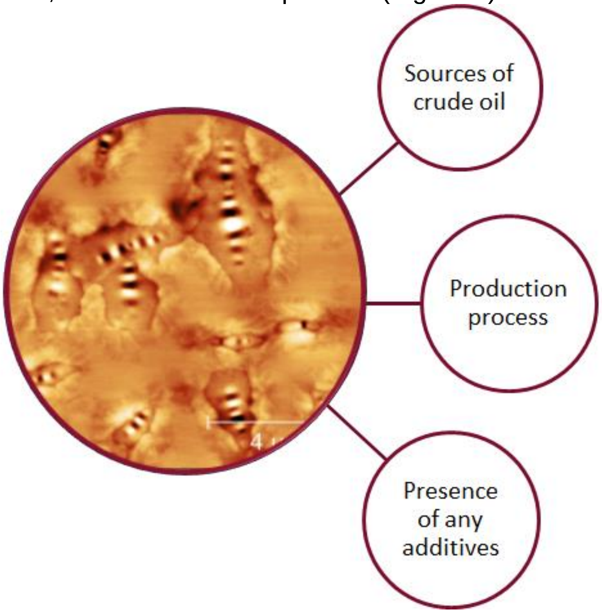


Figure 8: Bitumen microstructure and its relation to different parameters.

By cooling from the melt or liquid state of bitumen, a viscoelastic (semi) solid with a characteristic microstructural morphology emerges. The microstructure of bitumen has been investigated by using two different microscopic techniques, namely phase-contrast and polarized-light microscopy. These techniques showed the two-phase properties of bitumens [4, 20]. The investigators observed dispersed domains of few micrometers, and attributed the structure to be related to the saturate (crystalline) fraction of bitumen. Some researchers have used confocal-laser scanning microscopy to study a variety of bitumen microstructures and reported an existence of distinct elliptical domains of submicron to a few microns in size, dispersed in a matrix phase [21, 22].

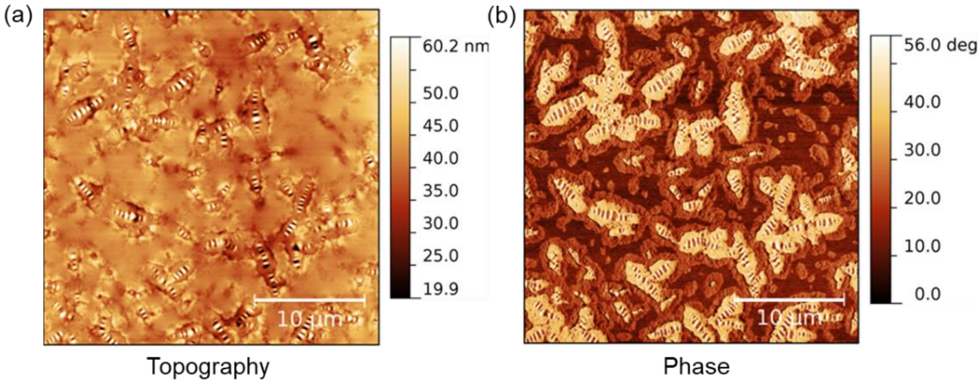


Figure 9: Bitumen microstructure as observed by atomic force microscope (AFM). 30×30 µm^2 AFM images of penetration 70/100 bitumen (a) topography image and (b) phase image (after [4]).

Detailed microstructure morphologies have been studied extensively over the past decade by using advanced imaging techniques like atomic force microscopy (AFM).

Microstructures investigated by AFM show evidence of a characteristic two-phase morphology as shown in Figure 9. In this two-phase morphology, elliptical domains commonly known as catana-phase or bee-structures are dispersed in a continuous matrix phase, also designated as the paraphase [20]. Some authors concluded that the bee-shaped structures consist of the most polar fraction in bitumen, namely the asphaltenes [21, 24, 25]. Others suggested a wax-induced phase separation in bitumen and attributed the crystallizing non-polar waxes as a component of these bee-structures [22]. More recently, the building blocks of bee-structures are believed to be a co-association of micro-crystalline wax and asphaltene fractions [4].

3.5 Agglomeration of asphaltenes in relation to metals and sulfur content:

Common building blocks of asphaltenes are highly condensed planar and polarizable polyaromatic ring systems of which many contain small amounts of heteroatoms (sulfur, nitrogen and oxygen) and trace quantities of metals [7, 8, 11, 14, 15]. Due to these features, molecules of this fraction are strongly associated with attractive forces. Asphaltenes are soluble in toluene and readily precipitate with the addition of a large excess of n-alkane [7].

Asphaltenes are chemically similar to the more resinous or polar components of bitumen. Sulfur in asphaltene molecules are found as a part of heterocycles like benzothiophene, dibenzothiophene, or residing in sulfide groups. From earlier potentiometric titration it is revealed that thiophenic sulfur is found in larger quantities in the resin fraction, as compared to the asphaltene fraction. Again, the amount of sulfide can vary in asphaltenes from different origins.

The asphaltene fraction of bitumen hosts most of the trace metals. The metals play an important role in the structure of asphaltene molecules. The type and concentration of metal also influences the association of asphaltene molecules and their aggregation characteristics.

Asphaltene molecular units with trace metals commonly form organometallic complexes, which are known to influence the size of the asphaltene molecules, and eventually self-associate to form larger structures. With an increasing concentration of metals, the molecular size of the asphaltenes increases, and as a result agglomeration becomes more evident. The size and structure of the asphaltene molecules influences the dispersion of these asphaltene particles within the matrix of bitumen and eventually impacts the rheological properties [7, 8, 11, 14].

Sulfur-containing compounds are also found in asphaltenes but their influence appears to be different compared to the metal-containing compounds. There is limited evidence showing that sulfur alone can facilitate agglomeration in asphaltene [8]. Hence, the role of sulfur in agglomeration behavior of asphaltenes is not conclusive from the literature

3.6 Heteroatoms, trace elements and asphaltene contents of SHRP bitumens:

The concentrations of the hetero elements (S, O, N), the most abundant trace metals, and asphaltene fraction of previously mentioned four bitumen from SHRP research are presented in Figure 10a, 10b, and 10c, respectively. The selection of these four bitumens are made on the basis of their distinctive sulfur content. Bitumen AAD-1 and AAK-1 are characterized by high sulfur concentrations (>6.0%), whereas AAM-1 and AAG-1 are low in sulfur (<2.0%).

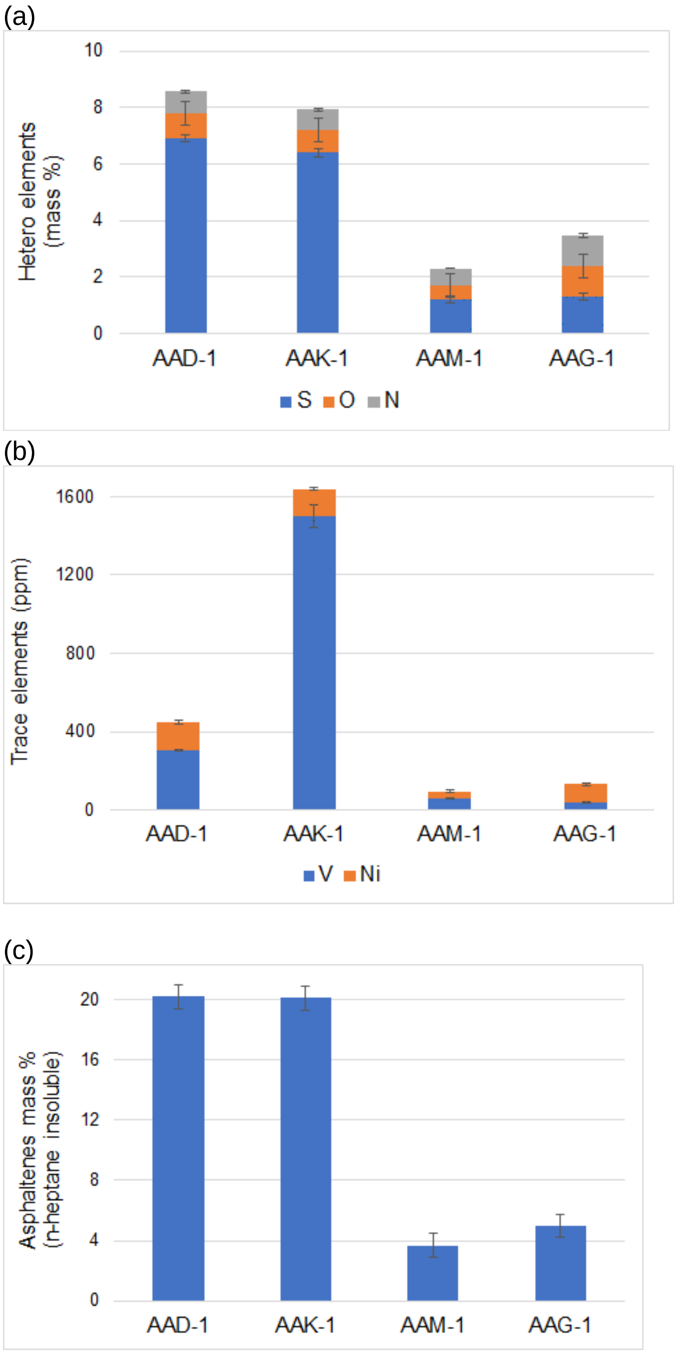


Figure- 10: (a) Hetero element (b) Trace metals and (c) Asphaltene contents of bitumen from SHRP research. [14[14]]

Additionally, bitumen AAG-1 is high in nitrogen compared to the other three bitumens. Oxygen values, range from 0.5 (AAM-1) to 1.1 (AAG- 1) mass %. Bitumen AAG- 1, and AAM- 1 are characterized by low metal concentrations.

The two high sulfur containing bitumens: AAD-1 and AAK-1 are rich in vanadium, where AAK-1 shows the highest vanadium content. AAG-1 is low in sulfur and metal content but contains more nitrogen and oxygen compared to the other bitumens. AAM-1 is low in all heteroatoms and also has low vanadium, and nickel content.

The bitumens containing high amounts of vanadium and nickel, are characterized with high asphaltene content. AAD-1 and AAK-1 are rich in sulfur, vanadium, nickel and also contain high asphaltene fraction. AAM-1 and AAG-1 have low vanadium and nickel concentration and are characterized with low asphaltene content, Figure 10b and 10c.

From the data analyses of the SHRP bitumen, it can be inferred that vanadium and nickel rich bitumens are identified with high amounts of sulfur and also asphaltenes [14]. It can generally be concluded that trace metals correlate well with the heteroatoms, especially sulfur, and also with the asphaltenes in bitumen.

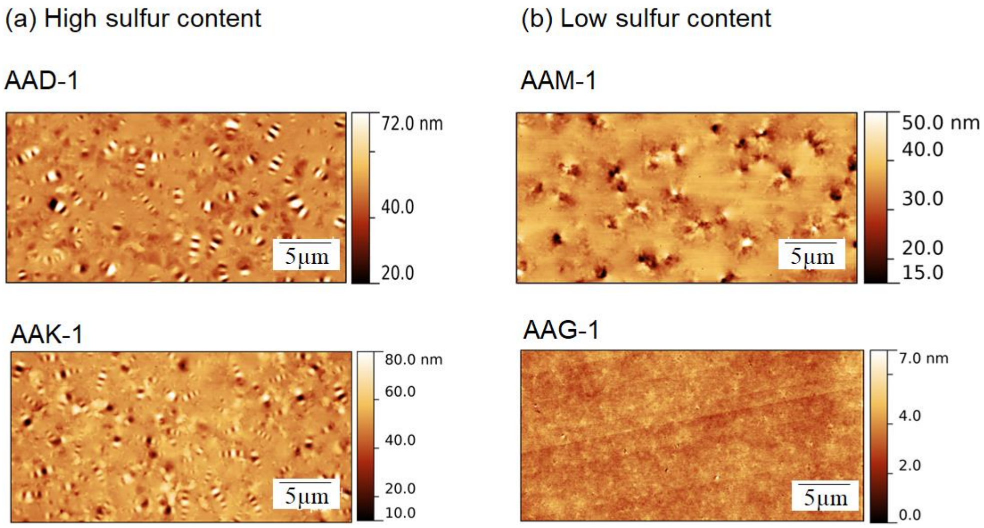


Figure 11: AFM micrographs of four core bitumens from SHRP research. 30×15m^2 topography images of (a) high sulfur (b) low sulfur containing groups of bitumen.[4]

Figure 11 presents AFM micrographs of the four core SHRP bitumen. Wherein Figure 11a and 11b show the microstructure of high sulfur bitumen (i.e. AAD-1, AAK-1), and bitumen of low sulfur content (i.e. AAM-1 and AAG-1), respectively. As seen from the earlier presented data, these bitumens are all different in their compositions such as asphaltenes, trace metals, and heteroatoms. The similar morphology of the closely packed domains of characteristic undulations for AAD-1 and AAK-1 are believed to be the co-association of wax and asphaltenes. As asphaltenes correlate well with the trace metals and sulfur content, high sulfur containing bitumen show more structuring due to their high asphaltene content. AAM-1 and AAG-1 don’t show this characteristic microstructure with undulations. AAM-1 shows some structuring due to its high (microcrystalline) wax content. These bitumens are low in sulfur, trace metals as well as asphaltene content.

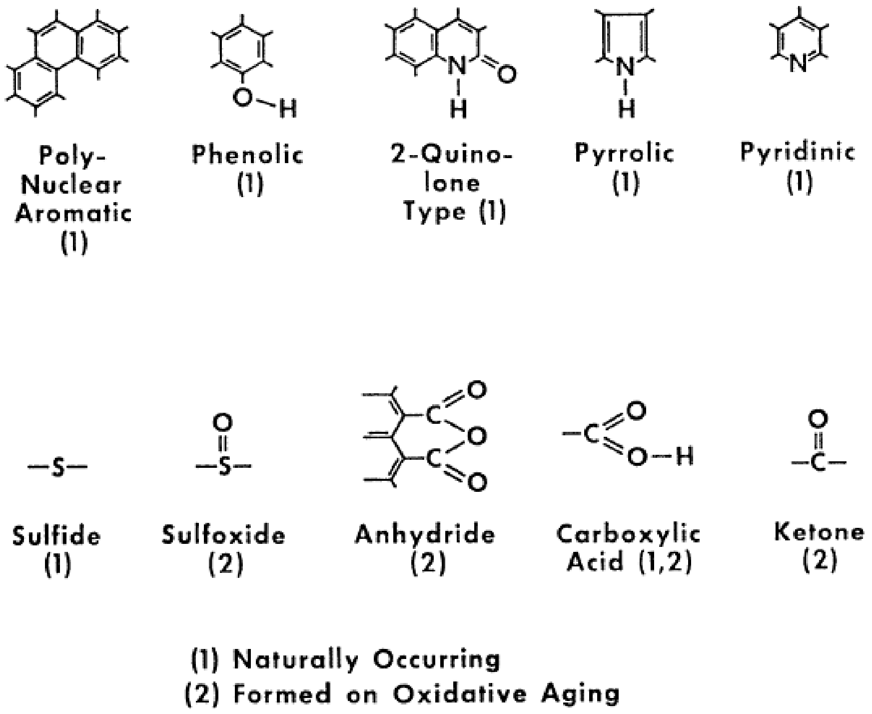


Figure 12: Functional groups in neat and aged bitumen measured by IR [14].

3.7 Oxidation of bitumen in relation to sulfur molecules

Sulfide groups present in bitumen are susceptible to oxidation into sulfoxides as shown in Figure 12. Oxidation of sulfide groups into sulfoxides can be characterized by a single band in the IR near 1,030 cm^{-1}. Organic sulfides are characterized as a bridging group between certain aliphatics and alkane backbones [15]. These bridging characteristics signify that these groups can hold together some high molecular-weight components such as the asphaltenes. With further oxidation sulfoxides turn into more polar sulfones and sulfonic acids, as shown in Figure 13, where the latter shows surface active properties.


(a) Cyclic sulfone

(b) Sulfonic acid

Figure 13: Successive oxidation of sulfoxides to more polar groups. (adapted from [15]).

The SHRP core bitumens have a total sulfur content ranging from 1% to 9%. A part of the total sulfur available in bitumen converts to sulfoxides during thermal oxidation at 50 to100°C. The data from the SHRP research using X-ray absorption near edge structure (XANES) and Electron Spectroscopy for Chemical Analysis (ESCA) revealed that aliphatic sulfide among the sulfur species is oxidized during the process of oxidation. Whereas, thiophenic sulfur (C4H4S) and aryl sulfide (C6H5S) are reported not to be affected during oxidation [14, 15, 17].

Figure 14 presents sulfoxide formation in different bitumens as a function of ageing time during PAV ageing, where the high and low sulfur bitumen groups are marked with orange and green, respectively. AAD-1 and AAK-1 are characterized with high quantities of sulfoxides. In AAG-1 and AAM-1 lower quantities of sulfoxides are detected compared to AAD-1 and AAK-1. AAM-1 contains the lowest amount of sulfide and also shows the lowest quantity of sulfoxide after oxidation.

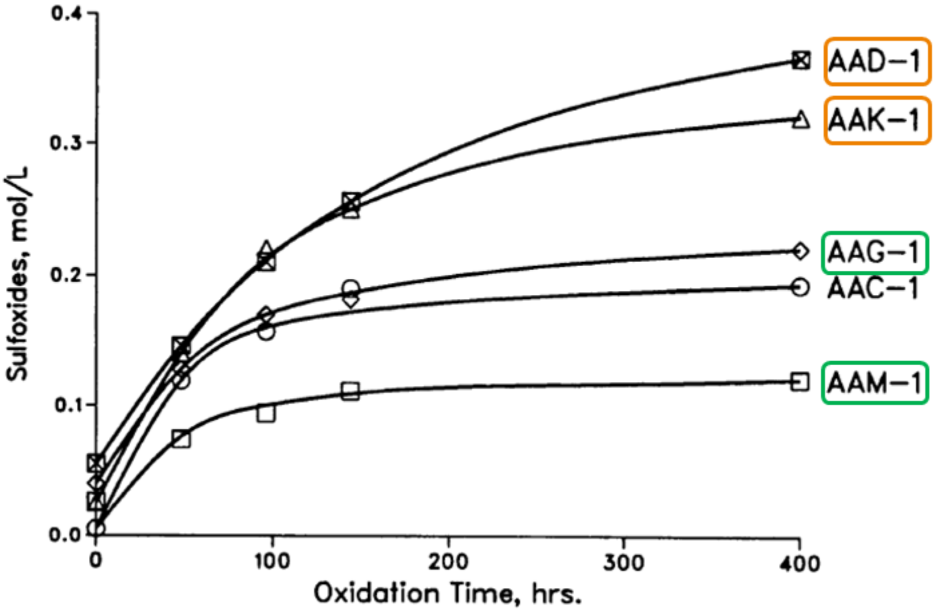


Figure- 14: Sulfoxide formation as a function of ageing time during PAV ageing at 60 °C [14].

The results reveal that sulfoxide formation as a function of time is different in varying bitumens during oxidation. It also demonstrates that bitumens with a similar total sulfur content but different aliphatic and aromatic distributions of sulfur can provide varying yields of sulfoxides. In low sulfur bitumens such as AAM-1 and AAG-1, aliphatic sulfide reacts rapidly and the formation of sulfoxide stops approximately after 30 hours of thermal oxidation. Bitumens that are high in sulfur in the form of aliphatic sulfide such as AAK-1 or AAD-1, oxidize longer and show higher quantities of sulfoxides. The rates of sulfide oxidation of the four core bitumens are similar, although they vary in sulfide content, vanadium and nickel contents. This suggests that sulfide and metal content don’t regulate the rate of oxidation, whereas other species like phenols or dihydroaromatic groups are believed to be influencing the rate of oxidation [14].

3.8 Influence of sulfur compounds on rheological and performance properties

The impact of sulfur on bitumen properties and performance mostly relates to the oxidation of sulfide into sulfoxide species, especially the conversion of aliphatic sulfides into their corresponding sulfoxides [17]. It is believed that sulfoxides introduce a strong hydrogen bonding, which influences other functionalities and the intermolecular interactions. This can lead to a change in the viscoelastic properties.

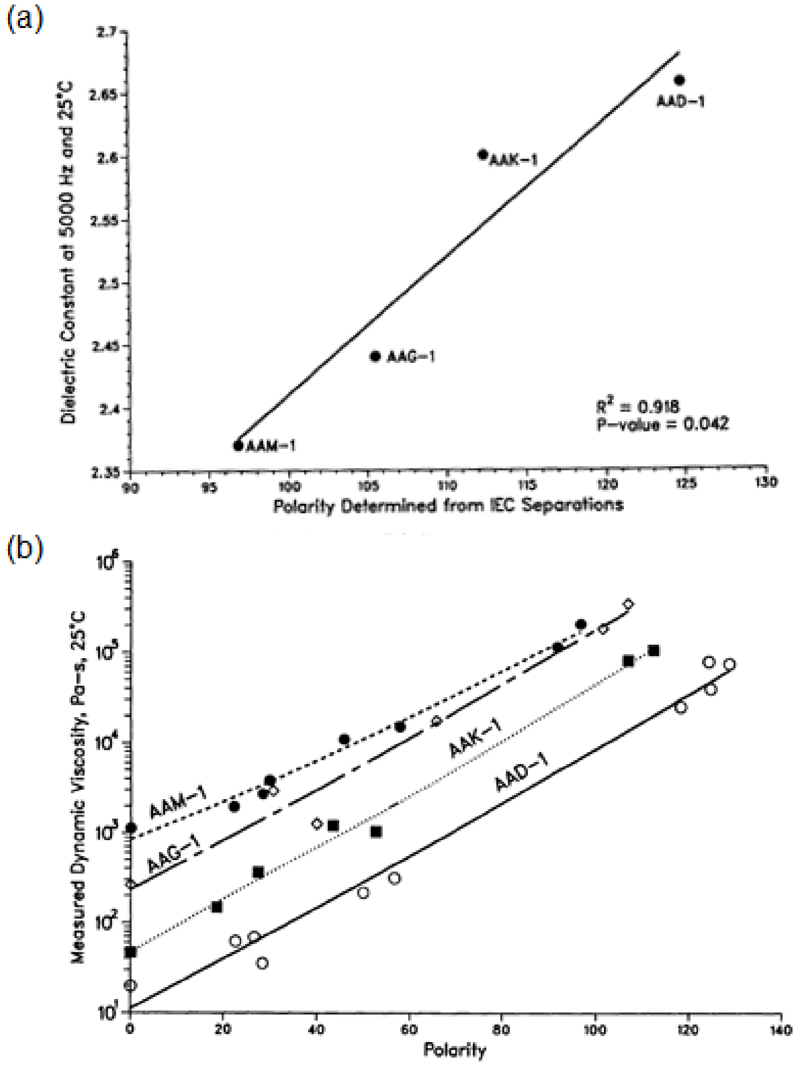


Figure 15: Polarity of the SHRP bitumens and their influence on viscosity. (a) Polarity of bitumen (b) Dynamic viscosity of IEC separations at 25°C as a function of polarity. [14]

Chemical composition influences the viscosity of bitumen. Figure 15a presents that higher sulfur-containing bitumen groups show a higher polarity than the lower sulfur bitumen groups. Figure 15b shows the viscosity at 25°C as a function of polarity, as determined from Ion Exchange Chromatography (IEC) separations for all four bitumens.
In this figure, viscosities of the IEC separations as obtained per bitumen are plotted against calculated polarities of the respective fractions. Details on calculation of polarities per fraction is found in the report SHRP-A-368 [14]. The linear relationships between viscosity and polarity suggests that the viscosity is determined by two factors, intercept and the polarity. Here intercept is the IEC neutral fraction. And polarity is determined by composition and relative amount of polar components in each bitumen.

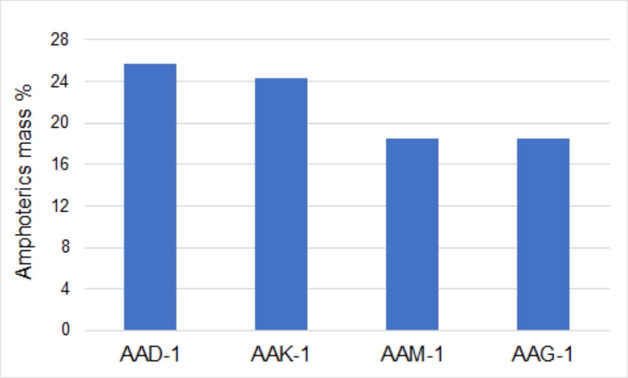


Figure 16: Amphoteric mass fraction in core SHRP bitumen [26].

From SHRP research it is concluded that the amphoterics, compounds that are able to react both as a base and as an acid, are responsible for most viscosity enhancement. Compounds containing polynuclear aromatic systems having one or more acidic groups and sulfoxide group are common amphoteric compounds in most bitumen [17]. Although the amount of amphoterics range from 18.5% to 25.7% of the total mass of these four bitumens (Figure 16), their contribution to the polarity ranges from 60% to 75% [14, 26]. Intermolecular hydrogen-bonding is one of the causative mechanisms for asphaltene association and may have a significant effect on molecular weight and eventually influences the viscosity of bitumen [8]. The formation of strong intermolecular hydrogen bonds between amphoteric species is known in literature and presence of such species in asphaltenes can potentially facilitate higher association [8]. The polarity of the bitumen determines its viscosity and also influences temperature susceptibility.

3.8.1 Ageing susceptibility and rheology of bitumen with varying sulfur

A selective oxidation of aliphatic sulfides into sulfoxides was used in SHRP research to assess and establish the possible link between sulfoxide formation and changes in the physical properties of SHRP bitumen. AAD-1 and AAG-1 bitumen contain 6.9% and 1.3% sulfur, respectively. The bitumen samples were oxidized at various temperatures and ageing times and the viscosity was measured subsequently.

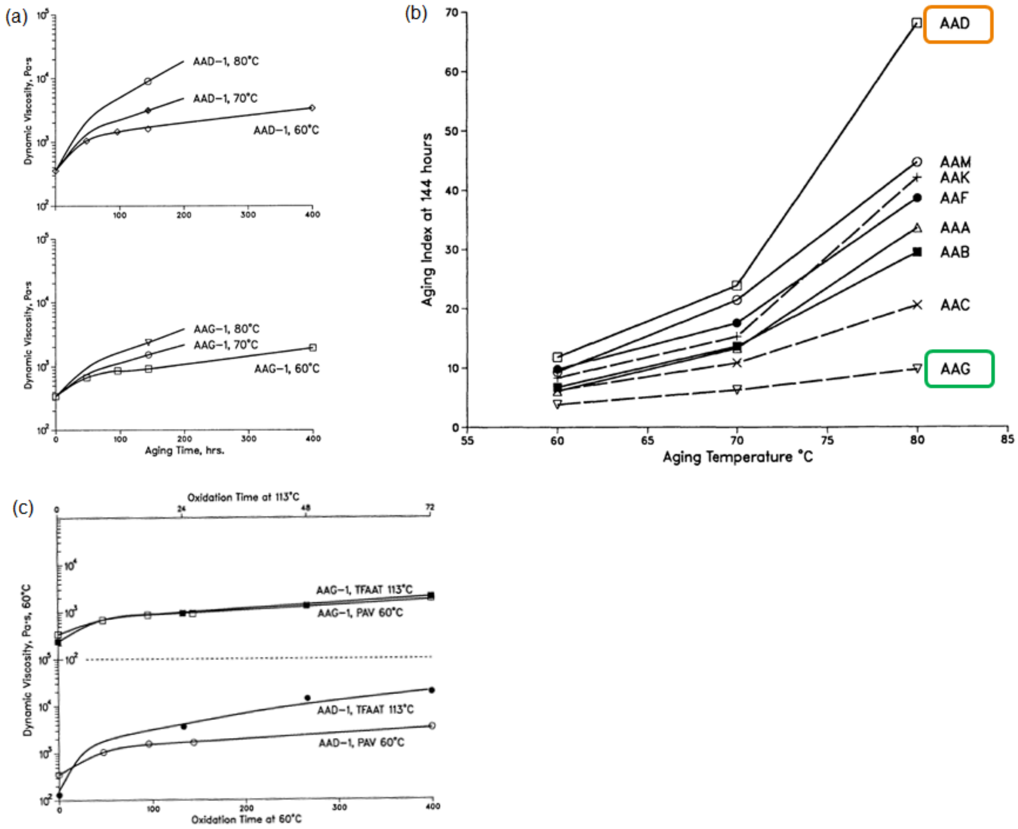


Figure 17: Ageing susceptibility of AAD-1 (high sulfur) and AAG-1 (low sulfur) bitumen as a function of time at different temperatures (a) PAV ageing at different temperatures (b) Ageing indices at different temperatures and (c) Influence of temperature on ageing kinetics. [14]

Figure 17 presents the influence of the temperature and the oxidation time on the bitumen viscosities. With increasing temperature, more oxidation takes place, resulting in a significant increase in viscosity. From the perspectives of the microstructural model, with increasing temperature, the polar associations within the bitumen disintegrate, which eventually allows for more bitumen molecules to react with oxygen. AAG-1 shows a slower rate of oxidation compared to the high sulfur-containing AAD-1 (Figure 17a). Figure 17b presents ageing indices of SHRP bitumen at three temperatures where bitumen AAD-1 and AAG-1 are marked. Here, the aging index is the ratio of viscosity after PAV aging conditions for 144 hours to the viscosity of bitumen prior to ageing at time zero. From the ageing indices it is apparent that the high sulfur-containing bitumen AAD-1 is more susceptible to ageing at different temperatures. Moreover, the temperature is an important factor that determines the rate and the extent of oxidation, as well as the resulting hardening of the bitumen. Figure 17c shows that high sulfur bitumen is more sensitive to temperature variation during oxidation as compared to the low sulfur bitumen. But ageing is a complex phenomenon and the susceptibility of a bitumen to ageing depends on other aspects of physical and chemical properties next to composition.

3.8.2 Pavement performance in relation to sulfur content of bitumen:

As discussed in the previous sections, oxidation of sulfides into sulfoxides increases the viscosity and consequently the hardness of the bitumen. It is also revealed that an increase in viscosity results into an increase in the concentration of amphoteric species [14, 26]. The increase in amphoteric species can potentially increase the susceptibility of the binder to stripping in the presence of moisture, and affect the strength of bitumen-aggregate adhesion properties.

The high sulfur-containing groups of bitumen AAD-1 and AAK-1 were determined to contain higher concentrations of oxidizable aliphatic sulphides. These bitumens were perceived to perform poorly with respect to different pavement damage mechanisms such as moisture damage, low temperature cracking. In contrast, the low sulfur-containing groups bitumen, AAM-1 and AAG-1, showed good performance in the field [14, 27]. Hence, there is a negative correlation of pavement performance in relation to low temperature cracking with oxidizable sulfur content in bitumen. Moreover, the maximum temperature to which the pavement is exposed is an important factor in determining the performance of the pavement as temperature is a crucial factor in ageing kinetics of bitumen and hence durability of asphalt. A small change in the pavement service temperature can result in different response properties of the bitumen with time.

4 Sulfur-extended bitumen (SEB)

The concept of treating bitumen with sulfur at high temperature has been around for more than a century. The first comprehensive study on sulfur modification of bitumen was reported by Benzowitz and Boe in the 1930s and showed that sulfur combines with bitumen, and showed improved properties over conventional bitumen [28, 29]. In the 1970s due to the increase in bitumen price, the concept of sulfur-extended bitumen (SEB) was further studied for upscaling. The US Bureau of Mines and the Federal Highway Administration developed SEB at a commercial scale [28, 30, 31].

At elevated temperatures, the incorporation of sulfur into bitumen releases hydrogen sulfides (H_2S) and sulfur dioxide (SO_2) gases, which raise health and safety concerns during production and application of asphalt. To address this issue, different methods to incorporate sulfur in pavements were developed for improving health and safety aspects. Incorporation of sulfur in bitumen continued to be used in the early 1980s as an alternative technology to modify bitumen and asphalt properties and to reduce bitumen consumption. Later, the use of sulfur declined due to its limited availability and significant increase in price, making the process uneconomical for the pavement sector.

Other developments on this technology include the solid palletization of sulfur in the late 1990s.These pellets can be directly added to asphalt mixtures, thus ensuring least exposure time of sulfur to the hot bitumen. In this way, the safety hazards associated with hot, liquid sulfur use can be eliminated, and the emissions stemming from the SEB asphalt mixture can be mitigated.

This chapter presents the interaction of elemental sulfur and its role as a modifier in bitumen properties. The chapter also discusses health and safety aspects associated with SEB technologies and some recent developments to mitigate emission-related hazards.

4.1 Chemical aspects of SEB

4.1.1 Interaction of bitumen and sulfur

Sulfur inside SEB can be found in three different forms: (1) chemically bonded, (2) 'dissolved' in bitumen, and (3) crystalline sulfur, which generally exists in the form of discrete tiny particles dispersed in the bitumen [28]. Characteristics of the molten sulfur influence the SEB properties, the phase transformation of sulfur as a function of temperature is rather a complex phenomenon. Elemental sulfur can exist in different forms in both the liquid and the solid state, where the atoms self-associate to form complicated systems of chain and/or ring structures. These transformations indicates that, sulfur can potentially exist in multiple phases during mixing, transport, and processing of SEB and asphalt hence influence their properties.

4.1.1.1 Chemically bonded sulfur

In SEB a part of the added sulfur chemically reacts with bitumen. In literature different ratios of chemically bonded sulfur were reported depending on the properties of the bitumen, the temperature and time during reaction (Figure 18). From the added quantity of sulfur, 20% up to 85% are reported to be chemically bonded with bitumen at a temperature below 150°C [28]. Sulfur reacts with hydrocarbons by introducing carbon-sulfur bonds, or by abstraction of hydrogen and subsequent hydrogen sulfide formation.

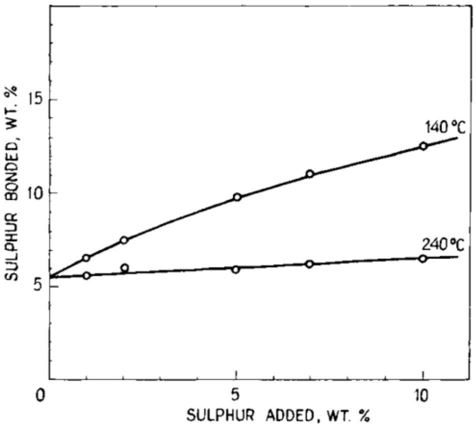


Figure 18: Influence of temperature on chemically bonded sulfur [28].

At a temperature range of 120–150°C, the naphthene-aromatic fraction in bitumen is known to be partially transformed into polysulfides. Dehydrogenation of the naphthene-aromatic fraction takes place at temperatures above 180°C, emitting hydrogen sulfide. If sulfur is blended at much higher temperatures like 240°C, naphthene-aromatics are transformed into asphaltenes through dehydrogenation and cyclization processes. Different bitumen samples treated with sulfur at 240°C can have a varied asphaltene content: several percent up to 40% asphaltene content are reported in the literature and the quantity of asphaltene formed depends on the composition of the original bitumen and the amount of added sulfur. [28, 30, 32, 33]. Such a chemical change increases the asphaltenes to resins ratio and the conversion depends on the overall composition of bitumen and the added quantity of sulfur. Eventually it introduces a change in the colloidal nature of bitumen by shifting towards a more gel-like structure.

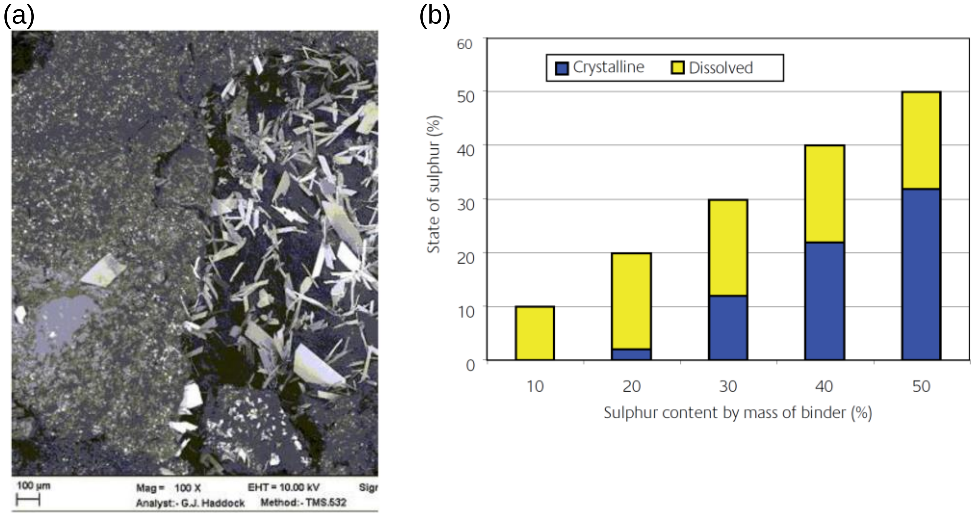


Figure 19 (a) Scanning electron microscopy micrograph of SEB showing structure of sulfur [5], (b) State of sulfur in SEB [34].

4.1.1.2 *Dissolved and crystalline sulfur*

Solubility of sulfur depends on the bitumen composition, temperature and time of mixing. Polysulfides that are formed due to the reaction of bitumen and elemental sulfur can further dissolve a part of the unreacted sulfur. In most SEB, sulfur has a

20% or higher solubility in the temperature range of 130-150°C. However, while being cooled, sulfur can recrystallize at ambient conditions as seen in Figure 19a [28, 30]. The residual sulfur is found as finely dispersed micro-crystals in bitumen and acts as a filler or stiffening component of the resulting binder. The relative amounts of dissolved and crystalline sulfur in SEB, as a function of added sulfur are presented in Figure 19b.

4.2 Influence of sulfur on performance properties of SEB

Sulfur modification impacts the mechanical properties of bitumen as well as the asphalt mixes. In SEB, sulfur can function as a binder component in bitumen or as a filler in asphalt. At low modification level, sulfur incorporates well with bitumen and mainly extends the binder rheological properties. Whereas, at higher modification, it acts as a filler and a structuring agent having a considerable effect on the mechanical properties of the asphalt mixture. The influence of sulfur on SEB properties are listed below:

- The density of binder increases with increasing amount of sulfur due to the higher density of elemental sulfur. This growth is more pronounced at sulfur content above 10wt%.
- Above the sulfur melting point, the viscosity of sulfur-extended bitumen is lower than that of pure bitumen. The viscosity decreases with sulfur content up to 15wt%, however further addition of sulfur increases the viscosity, surpassing the viscosity of the original bitumen at the sulfur content of approximately 56-60% [30, 32, 33].
- At low sulfur content in SEB, sulfur doesn’t influence the penetration index of the binder.
- The ring-and-ball softening point decreases with modification up to 10wt% sulfur content and then increases with further modification.
- Viscosity and softening point of SEB increase with the processing time.
- The Fraass breaking point increases a little with the increase of the sulfur content. Whereas others reported a decrease in the breaking point, showing poor correlation and hence the result is inconclusive.
- The influence of sulfur on the change in ductility of the binder is dependent on the temperature and the penetration of the original bitumen. Sulfur content up to 15wt% is reported not to show any concern on binder ductility.

The first test asphalt road, using SEB technology, was built in Texas in early 1934. Further pavements were laid in the 1970s in a number of European countries, as well as in the United States, Canada, and the Middle Eastern countries. The mixes can be produced using conventional paving equipment and in existing asphalt plants with only minor modifications. The performance of these pavements was tested under different climatic and traffic loading conditions [28].
Sulfur extended asphalt technologies are reported to have improved stability, deformation resistance, stiffness and fatigue performance. Some highlights on asphalt properties are given below:

- Sulfur-substituted asphalt mixes demonstrate higher fatigue lives than comparable conventional mixes.
- At the same loading time, the response of sulfur-containing pavements is more elastic compared to conventional pavements [31].

The addition of sulfur makes it possible for softer bitumen to be used in order to reduce low-temperature cracking without compromising the high-temperature deformation.
- SEB asphalt is resistant to plastic deformation and rutting at service temperature.
- SEB asphalt is reported to be less susceptible to moisture damage compared to conventional asphalt.

4.3 Environmental and safety aspects

4.3.1 Emissions and health related hazard during processing and application of SEB:

SEB processing at high temperature emits hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) which can cause significant health hazards. Evolution of H_2S is a function of temperature, time and amount of added sulfur. Figure 20 presents such a relationship between the emission of H_2S with mixing time and temperature. For SEB, the rate of emission is higher at temperatures above 150°C and a sulfur concentration above 1wt% of the blend.

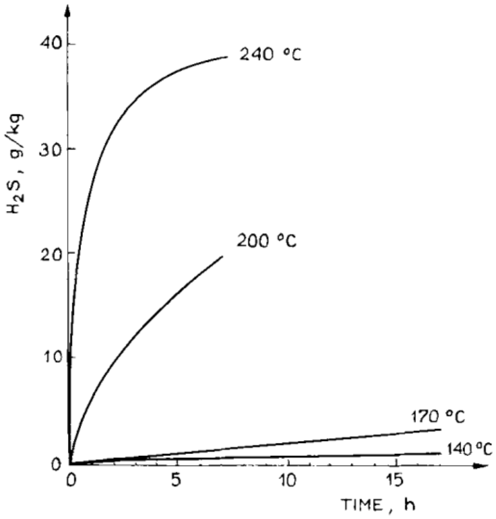


Figure 20: Hydrogen sulfide emission with temperature and reaction time for 95% bitumen (PEN 120-150) - 5% sulfur blend [28].

Emission levels are crucial for further evolving and acceptance of SEB technologies. Detailed experimental studies are carried out to assess the environmental impact of such technology in the whole value chain.

In several studies emissions were monitored at the location of SEB mixing, the asphalt mixing plant, and the paving site. High concentrations of H_2S are reported at the heated storage tanks and sulfur-unloading hopper. After application of asphalt, limited emission is monitored (0-4 ppm) at the paving site [28, 31]. All results show that emission and safety hazard in relation to this technology is integral and caution in processing, handling and application is required with a special attention to mixing temperature and time.

Within a detailed environmental assessment, soil- and water-quality measurements were carried out before and after road construction. The results indicated no detectable change in the sulfur content or pH-level [28]. Below 140°C the formation of hydrogen sulfide and sulfur dioxide is negligible. Hence, for improved safety measures, technologies should involve processing and operations at below 140°C.

4.3.2 Occupational safety

Safety of the workers is one of the major concerns for SEB technologies. Mixing of asphalt at high temperature (150°C), releases toxic and odorous H_2S and SO_2. Studies, with the focus on monitoring health and safety aspects and conditions of workers in close proximity to the labor carried out, checked for potential emissions. H_2S was monitored and detected in specific work areas where workers were positioned closest to the hot mixture. Appropriate temperature control during mixing is crucial in limiting H_2S emissions. In practice, the use of temperatures lower than 150°C during production of SEB, combined with personal protective equipment and monitoring devices are important[31].

Dust-related hazard is also reported where sulfur can precipitate as crystallites while cooled from vapor. This can cause sulfur to spread into areas beyond the production and construction sites [31].

Some literature reports that SEB asphalt mixtures can be recognized by a distinct odour, which is stronger than that of conventional asphalt [31- 34]. Eye irritation from sulfur vapor was detectable when workers without protective goggles were in very close proximity to the hot mixture.

Different countries adapt different upper limits of exposure for H_2S and SO_2. Commonly, the maximum allowable concentrations for H_2S and SO_2 have been settled at 20 ppm and 5 ppm, respectively. However, exposure to H_2S at the concentration of 20 ppm can cause irritation to eyes, and hence a lowering of the limits for H_2S to 10 ppm, and for SO_2 to 5 ppm were suggested and accepted by the American Governmental Conference on Toxicology and Health [28, 32, 33]. Currently the maximum accepted concentration for H_2S is also 10 ppm in the Netherlands, while the maximum exposure time is 8 hours [36].

4.4 Additive technologies to facilitate the use of SEB

The emission of hydrogen sulfide and sulfur dioxide can be reduced with the use of appropriate additives as well as by installing constructional protection. Several additives such as cupric oxide, ferrous a ferric oxide, sodium carbonate, aluminium oxide, and calcium chloride were found effective in reducing hydrogen sulfide emission. The addition of 1% of these additives lowers hydrogen sulfide emissions by approximately 50% [35].

Sulfur can also be added as pellets which may include wax additives to improve workability at lower asphalt mix temperature and also allows to obtain compaction properties at reduced temperature. Solid pellets and additives are directly introduced into the mixing drum. It melts rapidly to form part of the total binder around 115°C while keeping the mixing plant discharge temperature around 130°C.

5 IMO-2020 and its influence on choice of crude sources in bitumen refining

5.1 IMO 2020

The International Maritime Organization (IMO) has implemented a lower sulfur level for marine fuels, commonly known as IMO 2020, aiming to protect public health and the environment by reducing air pollution from marine fuels. This has a significant impact on both the shipping and the refinery industry and it is one of the key drivers for refinery transitions. The IMO act first came into force in 2005, and since then, the limits on sulfur oxide emissions have been progressively tightened. From 1 January 2020, the limit of Sulfur content in fuel oil used for ships is reduced from 3.5% to 0.50% w/w worldwide [2, 3].

5.2 Changes in different areas due to IMO 2020

The new regulation would impact the whole value chain: overall supply, availability of different products, transportation and pricing policy. The shipping industry can choose to use low sulfur fuels or invest and install scrubbers to treat or clean the exhaust gases from the ships. The refining industry is moving towards producing low or ultra-low sulfur fuels, which affects the choice of crude oil processed and changes in refinery configuration [1].

Due to the IMO 2020 legislation, refineries have to make choices on how to deal with the sulfur coming into the refinery via its crude oil. Refiners with a large yield of high-sulfur residue will look to pyrolysis of refinery residue and de-sulfurisation. This will have an impact on a range of products, including bitumen. Upgrading will reduce bitumen supply, and there is a risk that bitumen-producing refineries could close, as refiners move to lighter crude slates or install cokers and other upgrading capacity to produce lower-sulfur fuels and cut residue. This could lead to changes in bitumen grades or to supply tightness in some parts of the world during the peak paving season [1, 3].

There are visible trends that refineries produce increasingly harder grades than in the past, and IMO 2020 would likely reinforce the trend. This eventually may influence the price of softer grade bitumen.

As there are new crude sources and product streams being introduced in the course of time, knowledge at bitumen composition- and property-level become more important.

5.3 Transitions in refineries in relation to IMO2020

Refineries invest to adapt to a changing crude oil supply and market demand situations. Upgrading units are introduced in the refineries to process heavier, higher sulfur crudes, which typically attract higher discounts than lighter and lower sulfur, more easily processable crudes. In this way, over the years, refineries are adapting to more complex configurations to process a wider variety of crudes aiming at desired product yields. In most refineries, bitumen is not the primary product and the choice of crude oil will not primarily be based on the bitumen production. However, when the refinery produces bitumen, this is not by accident: a conscious choice is made. This choice comes with limitations to crude oil flexibility as the number of crude oils suitable for bitumen production is limited [1].

At the same time, recent refinery trends [37] show that more complex processes are becoming common, allowing feedstocks of different composition and consistency to be handled through upgrading and broadening of crude oil sources.

An individual refinery typically may process around 40 – 70 different types of crude oils. In the past few decades, new technologies, including both carbon rejection methods and catalytic conversion methods, have emerged. A combination of carbon rejection and the addition of hydrogen (H_2) can be used to upgrade residual fuels to make the low-sulfur gasoline and ultra-low-diesel (ULSD) fuels required by environmental regulations.

The upgrading of residual fuels uses either carbon rejection or H_2 addition, or a combination of the two. Traditional carbon rejection technologies include delayed coking, visbreaking, fluid coking, solvent deasphalting and residual fluid catalytic cracking [38]. Depending on the selected technique, a refinery has the possibility to upgrade and convert all vacuum residue in more marketable lighter products. Due to IMO 2020 several refineries have chosen to invest in upgrading to reduce the amount of heavy refinery products.

6 Upgrading of oil processing and its impact on sulfur content in bitumen

6.1 Bitumen manufacturing processes

Bitumen is primarily obtained in a refinery by vacuum distillation of carefully selected crude oil or blends of crude oil. Lighter, low molecular weight boiling point fractions from crude oil are separated, resulting in a product with high boiling point, high molecular weight and very low volatility. Depending on the specific refinery configuration and location, refineries process different crude oil blends to manufacture the oil products according to the market demand and select the most optimal mixture of crude oil types to match this market demand. On average, bitumen represents about 3% of the crude oil processed in refineries globally but this also includes refineries that choose not to produce bitumen [1].

As distillation residuum are the starting material for all bitumen production, the chemical and physical properties of the bitumen depend upon the properties of the crude oil from which the bitumen is manufactured. From commercially available assembly of crude oils or crude oil blends, only certain selections are suitable to produce bitumen.

In a simple refinery configuration, bitumen is produced using atmospheric distillation followed by a successive vacuum distillation, which is known as straight-run bitumen. Depending on bitumen product requirements, vacuum residue can be used directly as bitumen, processed further, or used as a component of blended bitumen [39].

6.2 Upgrading processes of vacuum residue

6.2.1 Deasphalting

A solubility-based separation unit; solvent deasphalting is used in some refineries for subsequent further upgrading of vacuum residues. The deasphalting process involves different solvents like propane, butane, isobutene, pentane, or supercritical solvent extraction to separate asphaltene-type fractions from the residue to produce lube oil base stocks. This process results in a harder bitumen grade than the original vacuum residue and can be blended with other bitumen components to produce required specified bitumen grades [1, 8, 39].

6.2.2 Oxidation

Another modification process of bitumen involves passing air through bitumen feedstock at elevated temperatures in order to significantly change the physical properties. Bitumen from such a process is known as oxidised or blown bitumen. The resulting product has an increase in softening point, decrease in penetration and an increase in viscosity which is required for some tailored industrial application [8, 11, 39].

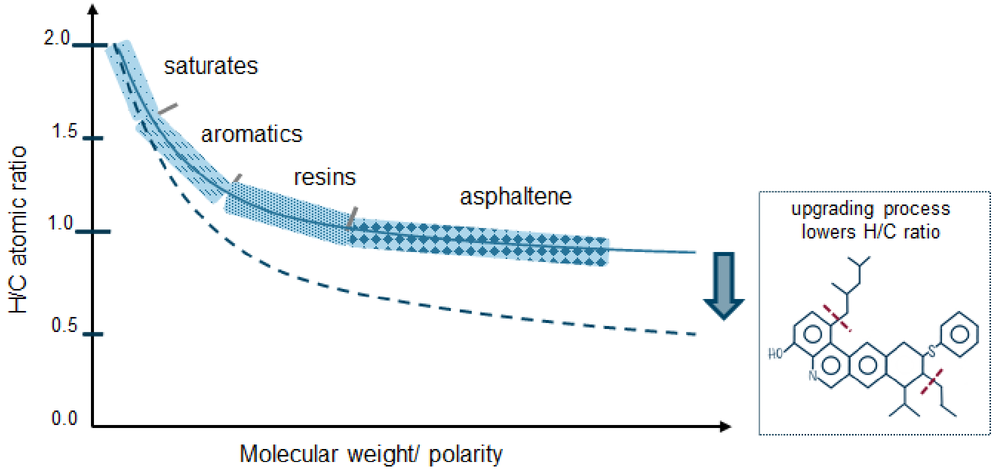


Figure 21: Change in the molecular classes in bitumen due to upgrading process

6.2.3 *Thermal cracking, Hydrotreating/ desulphurisation*

Refineries are equipped with other upgrading units that include a thermal cracking process to further break down the long paraffinic side chains attached to aromatic rings and subsequently transform them to form shorter molecules. Primary upgrading processes include thermal cracking, coking and hydroconversion. Operational temperatures for these processes are usually above 420°C to break C–C bonds at optimal rates. In a mild thermal cracking process like visbreaking, the vacuum residue is treated at high temperatures (440-500°C) and different process conditions depending on the properties of the feedstock, desired yield and end product requirements [39].

Hydrotreating takes place when hydrogen is introduced into this specific process usually resulting in desulphurisation. For bitumen production, after the process of thermal cracking the residue is introduced to a vacuum distillation unit to remove the lighter distillates. The residual product obtained through these processes is often a hard, highly viscous material that can be blended with other softer, low viscosity bitumen substances in the refinery to obtain a range of specific bitumen grades. Such processes produce bitumen rich in aromatic carbon. Hence reducing the hydrogen to carbon atomic ratio as shown in Figure 21.

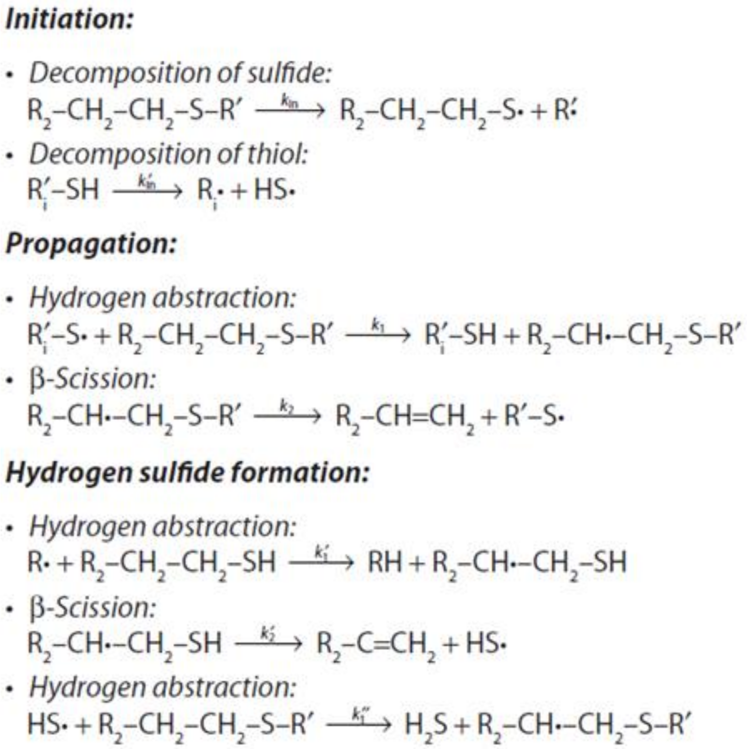


Figure 22: Example of reaction mechanism of sulfur during upgrading process.

6.3 The changes of sulfur compounds during upgrading process

Thiols, sulfides and disulfides sulfur species in bitumen are reactive under thermal process conditions. These species account for 50% of total sulfur in bitumen, whereas thiophenic sulfur compounds are stable and remain unaffected by thermal reactions.

Again, thermal reactions of sulfur are favorable because the C–S bond is weaker than other aliphatic bonds. Figure 22 shows an example of a reaction mechanism to illustrate the decomposition of sulfide with successive hydrogen abstraction. For example, disulfide bonds (RS–SR) are even weaker than sulfide (R–S) bonds. Hence, they are the bonds most likely to dissociate first and serve as initiators for the free-radical chain reaction [15].

Thermal processing of bitumen is always accompanied by the evolution of hydrogen sulfide, even at temperatures as low as 250°C. The facile rupture of sulfide bonds has been postulated as a major mechanism for cracking the high-molecular-weight components of bitumen. Thermal reactions of sulfur compounds can convert in the order of 30% of the sulfur in the bitumen without the aid of any catalyst, with an associated evolution of H_2S.

7 Conclusions

The review presents three aspects of the role of sulfur in bitumen. First, different sulfur species as present in bitumen are discussed. Detailed correlations between sulfur content and other compositional analysis such as hydrogen to carbon atomic ratio, heteroatoms and trace elements content are presented. The interaction of sulfur molecules with other elements and their relation to the evolution of microstructures and properties are also discussed. The influence of sulfur species in oxidation kinetics are also presented.
It is perceived that technical reports from the SHRP research are the most resourceful and contain well-comprehended information of complex compositional aspects to performance relationship of the binders. However, in the past three decades a lot has changed in bitumen manufacturing, from crude sources to the production processes. This has resulted in a more complex generation of bituminous products. We need to take a dedicated and multidisciplinary approach to address this challenge which needs immediate attention for developing knowledge at the material level to assess binder performance reliably.

Next, the influence of elemental sulfur in bitumen is discussed, where health and safety aspects are a bottleneck for such sulfur-extended bitumens. The influence of temperature and the time of mixing is crucial in this process to manage emissions. Improvements in properties at both binder and asphalt scales are reported, where there are ambiguities in some results. Further, IMO 2020 and changes in the refinery landscapes are discussed. The impact of IMO 2020 has still not been settled in terms of market dynamics, where changes in terms of choice or availability of crudes, manufacturing processes are foreseen that can influence bitumen properties.

The upgrading process is briefly discussed and reaction routes on how these thermal processes may decompose the sulfur-containing molecules are also presented.
This document linked the relationships of composition to bitumen and asphalt properties, with the focus on sulfur content. It also provides insights on the impact of ongoing changes in the bitumen market. It covers the following aspects as proposed in Task-1 ‘Mapping changes in binder properties in KPE plan of approach:

- Composition of bitumen from different origins and their role in performance.
- Oxidative ageing characteristics of bitumen in relation to composition.
- Transition in refineries and its impact on the production processes.
  - Upgrading of refineries.
  - Impact of IMO 2020 in refining process.
- Health, safety and environmental aspects in relation to bitumen manufacturing.

In this current scope, state of the art characterization methods for the evaluation of binders are not included and will be reviewed in the next phase in Task-1, KPE. In the follow-up literature review, the knowledge at the binder scale will be correlated with asphalt performance scale covering the following aspects:

- Production and operational properties during asphalt application.
- Health and safety during asphalt production.
- Performance related properties in relation to durability of asphalt.
- Recycling - rejuvenation potential of bitumen in asphalt application.

Finally, Task-1 will be closed with the proposal of a set of test methods for the evaluation of bitumen properties suitable for specific asphalt applications.

8 References

[1] S. Nahar, W. Teugels, A. van de Wall, N. Poeran, I. van Vilsteren, Grio on Bitumen: Mapping the Changes n Bitumen Market and its Impact on Performance, Proceedings of the 7th Eurasphalt & Eurobitume Congress v1.0, first published 1st July 2020, ISBN: 9789080288461.

[2] Sulphur 2020 – cutting sulphur oxide emissions, media centre- in focus, International Maritime Organization.

[3] Argus Media, https://www.argusmedia.com/en/blog/2019/september/11/imo-2020-series-beyond-the-bottomof-the-barrel.

[4] S. Nahar, Phase Separation Characteristics of Bitumen and their Relation to Damage-Healing, PhD Thesis, 2016. https://doi.org/10.4233/uuid:670c70ff-f9f0-4cdb-aa4d-b661e7117354.

[5] J. Read, D. Whiteoak, The Shell Bitumen Handbook (2003).

[6] P. Redelius and H. Soenen, Relation between bitumen chemistry and performance, Fuel 140, 34 (2015).

[7] J. C. Petersen, Chemical Composition of Asphalt as Related to Asphalt Durability, Asphaltenes and Asphalts, 2, Edited by T. F. Yen ,G. V. Chilingarian, Chapter-14, 2000. https://doi.org/10.1016/S0376-7361(09)70285-7.

[8] G.V. Chilingarian, T.F. Yen, Asphaltenes and Asphalts, 1, 1994.

[9] J.-F. Masson, L. Pelletier, and P. Collins, Rapid FTIR method for quantification of styrene-butadiene type copolymers in bitumen, Journal of Applied Polymer Science 79, 1034 (2001).

[10] J. Masson, Brief review of the chemistry of polyphosphoric acid (PPA) and bitumen, Energy & Fuels 22, 2637 (2008).

[11] A. Chakma, Kinetics and Mechanisms of Asphaltene Cracking During Petroleum Recovery and Processing Operations, Asphaltenes and Asphalts, 2, Edited by T. F. Yen ,G. V. Chilingarian, Chapter-6, 2000. https://doi.org/10.1016/S0376-7361(09)70277-8.

[12] P. Redelius, Asphaltenes in bitumen, what they are and what they are not, Road Materials and Pavement Design 10, 25 (2009).

[13] L.W. Corbett, Composition of asphalt based on generic fractionation, using solvent deasphaltening, elution-adsorption chromatography, and densimetric characterization, Analytical Chemistry 41, 576 (1969).

[14] J.F. Branthaver, J.C. Petersen, R.E. Robertson, J.J. Duvall, S.S. Kim, P.M. Harnsberger, T. Mill, E.K. Ensley, F.A. Barbour, J.F. Schabron, Binder Characterization and evaluation, Vol2: Chemistry, Technical Report SHRP-A-368 (1993).

[15] R. M. Gray, Upgrading Oilsands Bitumen and Heavy Oil, The University of Alberta Press, 2015.

[16] J. C. Petersen, Chemical composition of asphalt as related to asphalt durability: state of the art, Transportation research record (1984).

[17] J. B. Green, S. K.-T. Yu, C. D. Pearson, and J. W. Reynolds, Analysis of Sulfur Compound Types in Asphalt, Energy & Fuels 1993, 7, 119-126.

[18] S. N. Nahar, A.J.M. Schmets and A. Scarpas, Determining trace-elements in bitumen by neutron activation analysis, Proceedings 94th Transportation Research Board Meeting, Washington D.C., USA (2015).

[19] Qian, K.; Mennito, A. S.; Edwards, K. E.; Ferrughelli, D. T. Observation of vanadyl porphyrins and sulfur-containing vanadyl porphyrins in a petroleum asphaltene by atmospheric pressure photoionization Fourier transform ion cyclotron

resonance mass spectrometry. Rapid Commun. Mass Spectrom. 2008, 22, (14), 2153–2160.

[20] J. F. Masson, V. Leblond, and J. Margeson, Bitumen morphologies by phase detection atomic force microscopy, Journal of Microscopy 221, 17 (2006).

[21] F. Handle, J. Füssl, S. Neudl, D. Grossegger, L. Eberhardsteiner, B. Hofko, M. Hospodka, R. Blab, and H. Grothe, The bitumen microstructure: a fluorescent approach,Materials and Structures , 1 (2014).

[22] X. Lu, M. Langton, P. Olofsson, and P. Redelius, Wax morphology in bitumen, Journal of Materials Science 40, 1893 (2005).

[23]] D. A. Storm, E. Y. Sheu, and M. M. DeTar, Macrostructure of asphaltenes in vacuum residue by small-angle x-ray scattering, Fuel 72, 977 (1993).

[24] H. Groenzin and O. C. Mullins, Molecular size and structure of asphaltenes from various sources, Energy & Fuels 14, 677 (2000).

[25] L. Loeber, G. Muller, J. Morel, and O. Sutton, Bitumen in colloid science: a chemical, structural and rheological approach, Fuel 77, 1443 (1998).

[26] D. R. Jones, SHRP Materials Reference Library, Asphalt Cements: A Concise Data, Compilation, Technical Report SHRP-A-645 (1993).

[27] R. E. Robertson, J. Branthaver, H. Plancher, J. Duvall, E. Ensley, P. Harnsberger, and J. Petersen, Chemical properties of asphalts and their relationship to pavement performance, Tech. Rep. (Strategic Highway Research Program, National Research Council, 1991).

[28] I. Gawel, Sulphur-modified asphalts, Asphaltenes and Asphalts, 2, Edited by T. F. Yen ,G. V. Chilingarian, Chapter-6, 2000.

[29] J. Benzowitz and E.S. Boe, Effect of sulfur upon some of the properties of asphalt. Proc. ASTM, 38: 539 (1938)

[30] Kennepohl, G.J., Logan, A. and Bean, D.C., Conventional paving mixes with sulfur-asphalt binders. Proc. Assoc. Asphalt Paving Technol., 44: 485 (1975).

[31] N. Sakib, A. Bhasin, Md. K. Islam, K. Khan, M. I. Khan, A review of the evolution of technologies to use sulphur as a pavement construction material, International Journal of Pavement Engineering, DOI: 0.1080/10298436.2019.1612064.

[32] B. Celard, Sulfur addition to asphalt paving mixes, Eurobitume Seminar, London, p. 3 I8 (1978).

[33] Kennepohl, G.J. and Miller, L.J., Sulfur-asphalt binder technology for pavements. New Uses of Sulfur II. Adv. Chem. Ser., 165: 113 (1978).

[34] J. C. Nicholls, Review of Shell Thiopave™ sulphur-extended asphalt modifier, TRL Report, TRL672.

[35] Gawel, I., The selection of additives reducing the evolution of gaseous effluents during the preparation of sulphur-bitumen mixes. Int. Conf. Catalysis and Adsorption in Environmental Protection, Szklarska Poreba, Poland (1994).

[36] J. A. Knottnerus Hydrogen sulphide-Health-based recommended occupational exposure limit in the Netherlands, Health Council of the Netherlands.

[37] T. Janssens, T. Fitzgibbon, “The conundrum of new complex refinery investments.”, McKinsey & Company, September 2015.

[38] R. Elshout, “Upgrading the bottom of the barrel.”, Hydrocarbon Processing, March 2018.

[39] Asphalt Institute, and European Bitumen Association, The bitumen industry: a global perspective: production, chemistry use, specification and occupational exposure, 2015.

9 Signature

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