The role of sulfur in bitumen properties

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Summary
This paper 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 analyses 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 bitumen properties are discussed. Second, the influence of incorporating elemental sulfur in bitumen is discussed. Lastly, 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.

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 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.

Sulfur as naturally present in bitumen

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. Although bitumen molecules are composed predominantly of carbon and hydrogen, they commonly contain so called heteroatoms like nitrogen (≤2%), oxygen (≤2%) and sulfur (≤6%), and trace amounts of metals, mainly vanadium and nickel [1, 2, 3, 4].

SARA molecular fractions

To simplify the diversity of the chemical nature of bitumen, researchers took pragmatic approaches to separate bitumen into various chemical fractions. 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 1. The molecular weight, and the aromaticity of the fractions increase as saturates → aromatics → resins → asphaltenes [4, 5, 6, 7]. SARA fractionation can also be explained by the hydrogen to carbon atomic ratio, which decreases with increasing molecular weight (see Figure 1) [4, 5].

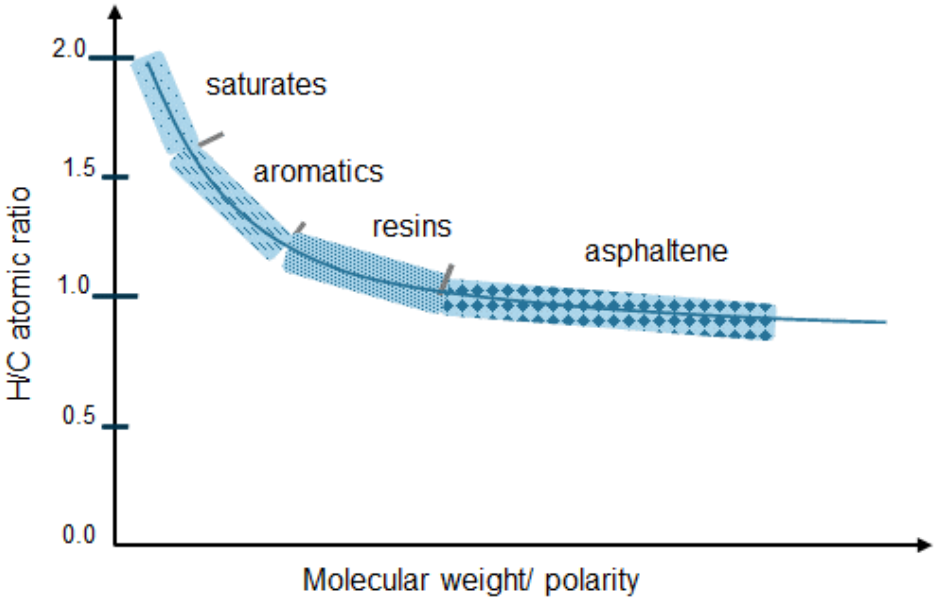
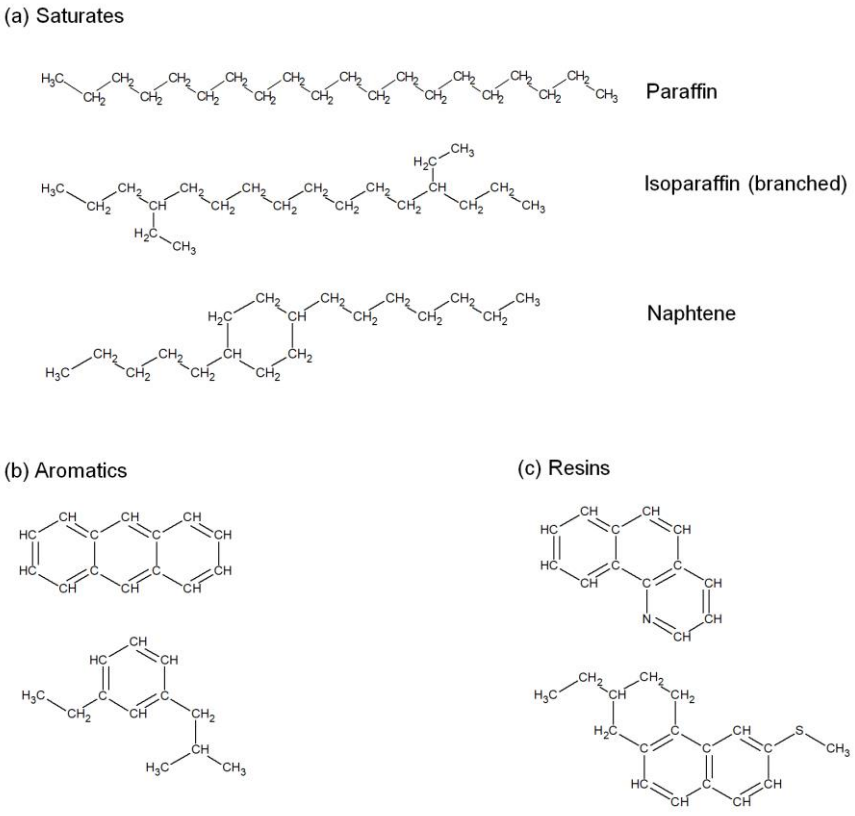


Figure 1: Schematic presentation of hydrogen to carbon atomic ratio of the SARA fractions of molecular classes of bitumen.

Saturates consist mainly of paraffins and naphthenes (saturated rings), Figure 2(a). The aromatic fraction is a mixture of paraffins, naphthenes and aromatic rings with sulfur containing compounds, Figure 2(b). Resins contain similar molecular classes as the aromatics, with multi-ring structures and heteroatoms (N, O, S), Figure 2(c). The asphaltene fraction consists of paraffins, naphthenes and aromatics composed into polycyclic structures containing heteroatoms [8] Figure 2(d).



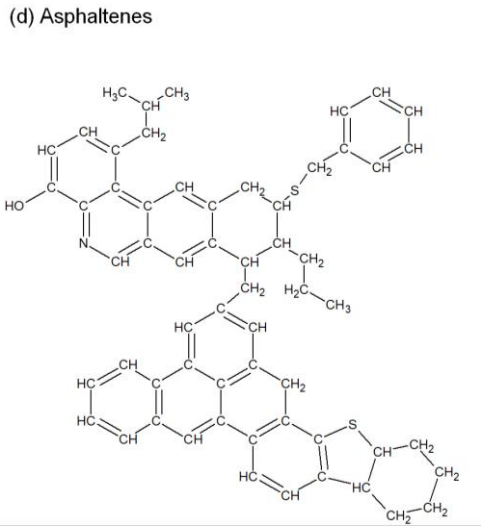


Figure 2: Representative molecular structures of bitumen SARA fractions. (after [5])

Elemental composition

Heteroatoms

Sulfur, nitrogen and oxygen are important components of bitumen, and are commonly known as heteroatoms which facilitate intermolecular interactions in the material. Sulfur is the most abundant heteroatom in most bitumen, although 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.

Neat bitumen does not contain sulfur or nitrogen in elemental form, but they instead are incorporated into certain functional groups. For example, sulfur is present in bitumen in the form of sulfides (R-S-R'), thiols (R-SH), and sulfoxides (S=O). Among these moieties, some groups result in polar interactions and hydrogen bonding due to their permanent dipoles resulting from inhomogeneous distribution of electrons. In neat bitumen sulfur is usually found to be distributed in all component fractions. However, in general the sulfur concentration increases from saturates → aromatics → resins → asphaltenes.

Trace metals

In order to understand some of the interactions between sulfur and other components in bitumen, we will now introduce another one of those components, namely the 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 heteroatoms as seen in Figure 3 [4, 9, 10, 11].

The effect of metalloporphyrins on bitumen oxidation properties were studied by several researchers in the past [4, 7, 9, 11]. 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. Concentrations of trace metals, especially vanadium, are a good indicator for the aging propensity of bitumen [7, 9, 11].

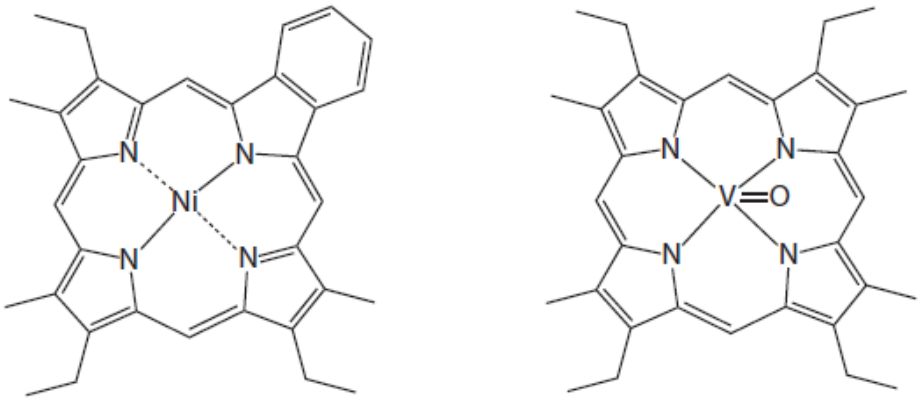


Figure 3: Nickel and Vanadium porphyrin structures in bitumen. [after 10]

Molecular interactions

Molecular interaction is the key that drives most of the structuring in bitumen. Commonly, molecules composed of carbon and hydrogen tend to associate with one another less strongly than molecules composed of hydrocarbons and the aforementioned heteroatoms [9].

The heteroatoms, although being a minor component compared to the hydrocarbon moiety, on the basis of their nature and electronegativity, can impart different functionalities and polarity to the molecules. 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 [3, 9, 12]. Heteroatoms induce an inhomogeneous distribution of electrons (i.e. permanent dipoles) and result in some polar interactions and hydrogen bonding. Polar groups such as for example carboxylic acids can interact directly with other polar groups, such as pyridine (an alkaline) groups to form salts. This strong association can drive asphaltene aggregation.

Agglomeration of asphaltenes

Extensive studies on composition and its influence on chemical and physical properties of bitumen were performed in the Binder Characterization and Evaluation project within the Strategic Highway Research Program (SHRP) in US [9]. In this SHRP research, four bitumens were selected for their distinctive sulfur content. The concentrations of the hetero elements (S, O, N), the most abundant trace metals, and asphaltene fraction of these bitumens are presented in Figure 4a, 4b, and 4c, respectively. 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%).

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 [9]. It can generally be concluded that trace metals correlate well with the heteroatoms, especially sulfur, and also with the asphaltenes in bitumen.

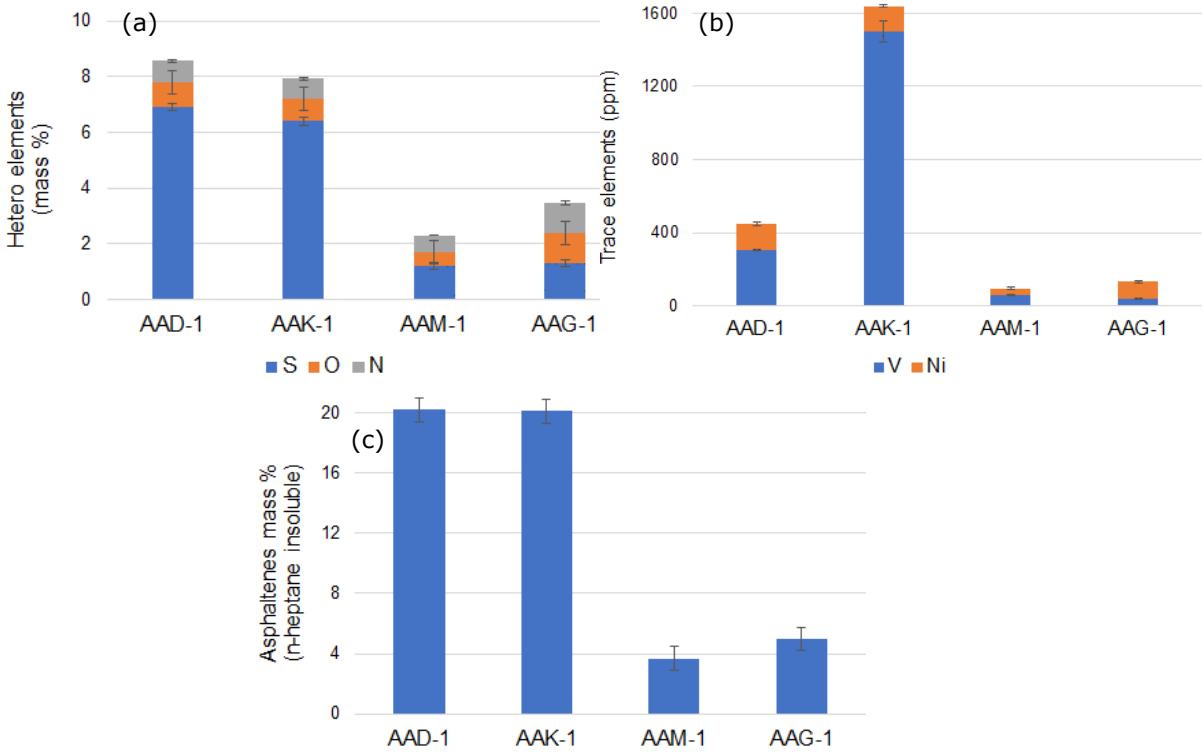


Figure 4: (a) Hetero element (b) Trace metals and (c) Asphaltene contents of bitumen from SHRP research. [9]

The asphaltene fraction of bitumen hosts most of the trace metals. Asphaltene molecular units with trace metals commonly form organometallic complexes (see also figure 3), 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 [3, 4, 7, 9].

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 [4]. Hence, the role of sulfur in agglomeration behavior of asphaltenes is not conclusive from the literature.

Sulfur and oxidation of bitumen

Sulfide (R-S-R) groups present in bitumen are susceptible to oxidation into sulfoxides (S=O). With further oxidation sulfoxides turn into more polar sulfones ($S(=O)_2$) and sulfonic acids ($R\text{-}S(=O)_2OH$). Figure 5 presents sulfoxide formation in different bitumens as a function of ageing time during PAV (Pressurized Aging Vessel) ageing, where the high and low sulfur bitumen groups are marked with orange and green, respectively.

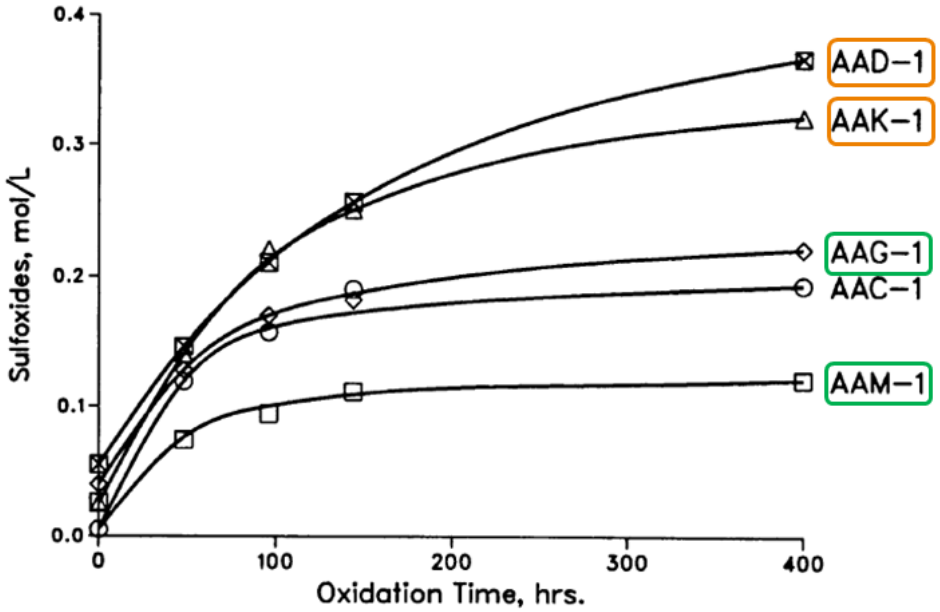


Figure 5: Sulfoxide formation as a function of ageing time during PAV ageing at 60 °C [9].

The results reveal that sulfoxide formation as a function of time is different in varying bitumens during oxidation. 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 aliphatic sulfide such as AAK-1 or AAD-1, oxidize longer and show higher quantities of sulfoxides. The rates of sulfide oxidation of the bitumens are similar, although they vary in sulfide, vanadium and nickel contents. This suggests that sulfide and metal content don't regulate the rate of oxidation [9].

Temperature is also an important factor that determines the rate and the extent of oxidation in bitumen, as well as the resulting hardening of the bitumen. When the temperature is elevated, the polar associations within the bitumen disintegrate, which eventually allows for more bitumen molecules to react with oxygen. High sulfur-containing bitumens appear more susceptible to ageing at different temperatures, as compared to low sulfur-containing bitumens. 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.

Influence of sulfur on 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 [13]. Figure 6a presents that higher sulfur-containing bitumens show a higher polarity than the low-sulfur bitumens. Figure 6b shows the viscosity at 25°C as a function of polarity for all four bitumens. The linear relationships between viscosity and polarity suggests that the viscosity is determined by two factors, intercept and the polarity.

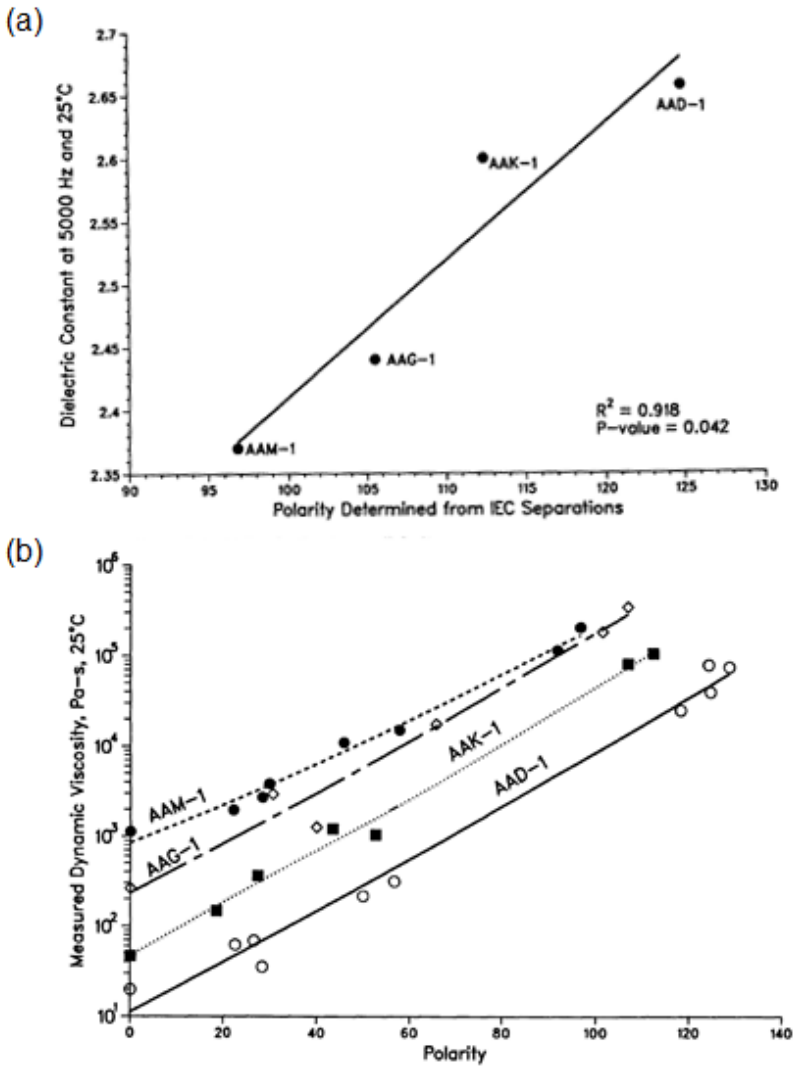


Figure 6: Polarity of the SHRP bitumens and their influence on viscosity. (a) Polarity of bitumen (b) Dynamic viscosity of IEC separations at 25°C as a function of polarity. [9]

The high sulfur-containing groups of bitumen were perceived to perform poorly with respect to different pavement damage mechanisms such as moisture damage and low temperature cracking. In contrast, the low sulfur-containing groups bitumen showed good performance in the field [9, 14]. Hence, there is a negative correlation of pavement performance in relation to low temperature cracking with oxidizable sulfur content in bitumen.

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 [15, 16]. In the 1970s due to the increase in bitumen price, the concept of sulfur-extended bitumen (SEB) was further studied for upscaling. Later, the use of sulfur declined due to its limited availability and significant increase in price.

Chemical aspects of SEB
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 [15]. 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 indicate that sulfur can potentially exist in multiple phases during mixing, transport, and processing of SEB and asphalt, and thus influence their properties.

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:

- 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 [17, 18, 19].
- 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.

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. 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 [20, 21].

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 [21, 22].

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.

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

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 [22]. 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 [23].

Upgrading processes of vacuum residue

Deasphalting

A solubility-based separation unit; solvent deasphalting is used in some refineries for subsequent further upgrading of vacuum residues. 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 [4, 22, 23].

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 oxidized 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 [4, 7, 23].

Thermal cracking, Hydrotreating/desulfurisation

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 [23].

Hydrotreating takes place when hydrogen is introduced into this specific process usually resulting in desulfurisation. 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.

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. Thermal reactions of sulfur are favorable because the C–S bond is weaker than other aliphatic bonds. Thermal processing of bitumen is always accompanied by the evolution of hydrogen sulfide (H_2S), 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.

Conclusions

This paper discussed the presence of natural sulfur in bitumen, and its relation to other bitumen components, most prominently the asphaltenes and trace metals. Sulfur in bitumen molecules induces polar interactions, which promote the agglomeration of asphaltenes. Also, most sulfur groups in bitumen tend to oxidize more readily than other functional groups in the bitumen, allowing for even more polar interactions. We show a relationship between increased polarity, and an increase in viscosity as is observed in bitumens. However, it remains hard to directly relate these observed behaviors to the presence of sulfur alone, as sulfur content tends to increase together with asphaltene and trace metal contents.

We've also discussed the influences of adding elemental sulfur to a bitumen, referred to as SEB, which at low concentrations changes primarily the rheological properties, whereas in higher concentrations it will act as a filler, also changing the mechanical properties. Lastly, we've discussed changes in today's bitumen market in relation to changes happening at oil refineries, as there are visible trends that refineries produce increasingly harder grades than in the past.

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