Fuel 140 (2015) 34–43

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Relation between bitumen chemistry and performance

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HIGHLIGHTS

- Interactions between hydrocarbon molecules is very important for the physical properties of the product.
- The strength of some of the interactions may be estimated by solubility parameters.
- Large aromatic systems contribute with important interactions not determined in the solubility parameters.
- The viscosity of a heavy petroleum product may be estimated from molecular weight and aromaticity.
- The behaviour of the fractions "asphaltenes" may be explained in terms of molecular interactions.

ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form 30 July 2014
Accepted 11 September 2014
Available online 1 October 2014

Keywords:
Bitumen
Interactions
Chemistry
Asphaltenes
Viscosity

ABSTRACT

The relation between the chemical composition of bitumen and the physical properties, such as viscosity or viscoelasticity is very important for the use of bitumen as an advanced construction material. In view of the limited understanding of the exact molecular structure of the millions of different molecules constituting bitumen, many different proposals for the structure of bitumen have been published over the last 100 years. In this paper we propose that interactions between the molecules are the main determinants for the physical properties of bitumen. We discuss different types of interactions, typical for hydrocarbons, such as dispersive London interactions, polar interactions and pi–pi interactions, and how the strength of the interactions may be estimated by different methods. We also discuss one class of molecules in bitumen, defined by non-solubility, the asphaltenes, and why they contribute strongly to the thickening effect of bitumen, but we also conclude that asphaltenes are not the only molecules contributing to viscosity. Finally we show how the use of molecular parameters like molecular weight and aromaticity can be used to give a good estimate of the viscosity of heavy hydrocarbons of different composition.

1. Introduction

Bitumen is a black adhesive material produced from crude oil. The most common use is as the binder in asphalt. But it is used for many other purposes, including roofing applications and other types of water tightening as well as many other applications. Long before crude oil started to be produced (1859) bitumen was found in nature as "natural asphalt" in many places around the world. The very extensive use of asphalt developed in parallel to the enhanced demand of good roads to meet the growing use of cars in the society.

Ever since the production of bitumen as a distillation residue from petroleum, there have been attempts to clarify the true chemical structure of bitumen. It was very soon stated that bitumen consists mainly of hydrocarbons with small amounts of heteroatoms including sulphur, nitrogen and oxygen and traces of metals such as vanadium, nickel and iron. In the early days (1924) Nellensteyn speculated that bitumen was a colloidal dispersion of carbon particles dispersed in oil [1]. The chemistry of bitumen has sometimes been considered to be a mystery and "very complicated". When consulting literature, among relevant and high class investigations, also unsupported speculations and misinterpretations have been published. It is not always easy for the newcomer to navigate between contradictory claims and statements.

It has sometimes been assumed that once we know the chemistry of bitumen we will be able to predict its performance as a construction material, as well as specify the properties of "good"

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http://dx.doi.org/10.1016/j.fuel.2014.09.044
0016-2361/

bitumen. However, the knowledge about the molecules is only of limited help for understanding bitumen, and advanced modern analytical techniques always provide average results which are not easily translated to physical properties or performance properties. Instead separation techniques have been used to divide bitumen into fractions. Many techniques, using different properties of the molecules for separations have been used. These fractions have then been correlated to physical properties sometimes rather successful but more commonly without finding any general correlation. The fractions are generally very heterogeneous and are only defined by the method of separation. There is no "gap" in chemical properties between the fractions. A common misunderstanding is to consider the fractions as "the components in bitumen" and claim that bitumen consists of a mixture of three, four or five types of compounds instead of a continuum of molecules. The continuum consists of relatively large hydrocarbons with different size, polarity and aromaticity. The smallest size of the hydrocarbons is defined by the processing conditions of the crude oils (cut point in the vacuum distillation tower) and the largest size is defined by the crude oil.

In this paper we will give an explanation how the chemistry of bitumen determines the physical properties and performance properties of the bitumen as a construction material in asphalt.

2. Bitumen at a molecular level

Today the chemistry of the molecules constituting bitumen can be considered to be fairly well known although more than 95% of the molecules have never been isolated or identified and can thus be said to be unknown to mankind. How can we then claim that the chemistry is well known? One pragmatic way of estimating the chemistry of bitumen is to study the composition of the lighter fractions from crude oil, the distillates. The light distillates with the lowest boiling points are well known in detail, while the composition of the heavier distillates is only known in more general terms. The fact that bitumen is a residue does not mean that the principle structure of the molecules changes during the transition from a distillate to a residue. It is just that the molecules become larger and thus have a higher boiling point. Some contributions to the new chemistry are collected in Ref. [2] and further detailed information about the chemistry of the molecules can be found in a series of references by McKenna et al. [3–5]. All these results confirm the theory which was already presented in the 1980s by Boduszynski et al. [6] but which attracted limited attention.

All molecules in bitumen are hydrocarbons with small amounts of sulphur, nitrogen and oxygen and traces of metals like vanadium and nickel. The hydrocarbons may be described by a number of core structures consisting of polyaromatic structures containing different number of fused rings, saturated polycyclic structures also with different number of rings and combinations of these. All these core structures contain saturated hydrocarbon side chains of different chain length and different substitution patterns. The number of possible isomers is almost unlimited. That is the reason why bitumen consists of millions of different molecules, almost none of them in sufficiently large quantities that it is possible to isolate and characterize them. So even if the structure is known in principle, the exact structure is unknown. Based on average analytical data it is possible to suggest an average "bitumen molecule" as illustrated in Fig. 1. The molecule has never been proven in crude oil or bitumen, but if it exists it will fall in the bitumen fraction. The size is large enough to give a boiling point above the cut point for the most heavy distillate, it contains sulphur in thiophenic structure, which is the most common structure for sulphur based heterocyclic molecules, and it contain aromatics and saturates in approximately the average amount known for bitumen.

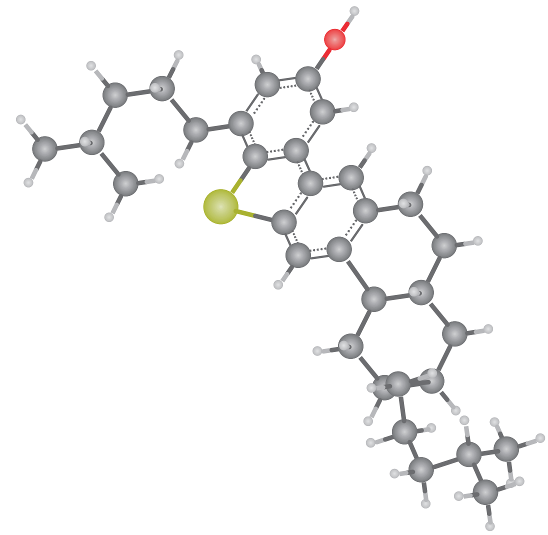

Fig. 1. "Typical" bitumen molecule.

The smallest size of the bitumen molecules varies depending on type of crude oil and grade of bitumen. It is determined by the cut point at the distillation of the crude oil. It is possible to estimate that the smallest size of the molecules is around 20 carbons and goes up to the largest size in the residue. This is still under discussion among researchers and there are a lot of different opinions. Based on the latest findings [2–5] it seems unlikely that there are any significant quantities of molecules larger than about 1500 g/mol (about 110 carbons).

The most typical chemical property of bitumen is its heterogeneity, particularly the unique combination of the large number of similar but still different molecules, which makes it meaningless to describe bitumen with one or a few "typical" average molecules, but the whole range of molecules must be taken into consideration to make realistic chemical description of bitumen.

3. Separations

Traditional analytical techniques like ultraviolet spectroscopy (UV), infrared spectroscopy IR, nuclear magnetic resonance NMR, or mass spectroscopy MS have given substantial information about the average chemical composition of bitumen. Most bitumens give more or less identical spectra and no general correlations between physical properties and any particular functional group as identified by the techniques above are known. The only technique which has been frequently used is IR, which permits identification of carbonyls and sulphoxides formed as a result of ageing. Instead different techniques to separate bitumen into fractions have been developed. Over the years many different techniques based on different separation principles have been tried. Some examples are:

• Reactivity with sulphuric acid	Rostler Sternberg [7]
• Solubility	Hoiberg [8]
• Size (SHRP SEC separation)	SHRP report [9]
• Charge (SHRP IEC separation)	SHRP report [10]
• Polarity (SARA)	Several different procedures [11]

Today the most popular technique is the separation into saturates, aromatics, resins and asphaltenes (SARA). There are several different techniques claiming to do the same separations, for