Full Length Article

A study of the combustion chemistry of petroleum and bio-fuel oil asphaltenes

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HIGHLIGHTS

- Py-GC–MS of asphaltenes suggests a structure of linked small aromatic and naphthenic units.
- Py-GC with AED was used to track the behaviour of S, N and V.
- A mechanism of soot and cenosphere formation is given.
- The analogous bio-asphaltenes have been studied in a similar way.

ARTICLE INFO

ABSTRACT

The combustion of heavy fuel oils such as Bunker C and vacuum residual oil (VRO) are widely used for industrial applications such as furnaces, power generation and for large marine engines. There is also the possible use of bio-oils derived from biomass. Combustion of these oils generates carbonaceous particulate emissions and polynuclear aromatic hydrocarbons (PAH) that are both health hazards and have an adverse effect on the climate. This paper explores the mechanism of the formation of fine particulate soot and cenospheres. The chemical structure of petroleum asphaltene have been investigated via pyrolysis techniques. The results are consistent with a structure made up of linked small aromatic and naphthenic clusters with substituent alkyl groups, some in the long chains, with the building blocks held together by bridging groups. Other functional groups also play a role. The corresponding bio-asphaltene is made up of similar aromatic and oxygenated species and behave in an analogous way.

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1. Introduction

Heavy fuel oils (HFO), such as Bunker C and vacuum residue (VRO), and increasingly bio-oils, are commonly used as fuel for industrial boilers, power generation, and as transport fuels particularly in large marine engines for container ships. The combustion of these oils can give rise to particulate emissions which, along with associated gaseous sulphur and nitrogen oxide pollutants have an adverse environmental effect [1–3].

Heavy fuel oils are burned as sprays with individual droplets up to 1 mm diameter in large combustors. On entering a hot combustion chamber the lighter components evaporate and ignite the droplets which then burn. The heavier components in the droplet thermally decompose to form a carbonaceous char or cenosphere and fine particulate soot. The extent of their formation during the combustion of heavy oils is associated with the asphaltene content. This is defined [4,5] as the oil fraction insoluble in an n-alkane solvent such as n-heptane but soluble in an aromatic solvent such as toluene; attempts have been made [4] to characterise asphaltenes in general from their number-average molecular weight, M_n, their content of heteroatoms, and their degree of aromatic condensation. Asphaltenes from bio-oils may be considered similarly [6,7].

Such approaches are consistent with the differences between the 'average structures' for petroleum asphaltenes which have recently been suggested and which can have a strong influence on how asphaltenes affect heavy oil combustion and its environmental impact. Thus, two markedly different structural types have been proposed [8,9]: one, the 'continental' or 'island' structure in which a single aromatic core containing approximately seven rings is substituted with pendant groups, especially long-chain alkyl groups, and a second, termed the 'archipelego' in which small naphthenic and aromatic groups ranging from monocycles upwards are joined together by alkyl and heteroatomic links [10,11]. A single asphaltene sample may contain mainly one structural type but

may contain significant amounts of another. For example, Morgan et al. [12] isolated solvent sub-fractions from the Maya asphaltene which nuclear magnetic resonance (NMR) analysis suggested differed in average structure, especially in the degree of condensation of the constituent aromatic nuclei. On the other hand, the major contribution of 'archipelago' structures has been suggested by Herod et al. [9] and by Waller et al. [13] on the basis of Py-GC experiments; further, Karimi et al. [11] pyrolysed thin films of asphaltene which yielded the constituent 1–4 aromatic ring molecular 'building blocks' apparently from 'archipelago' structures, whereas the 'island' structures might be expected to produce more condensed molecules. The overriding importance of structures with smaller aromatic units was again emphasised by Karimi et al. [11].

Much recent work on asphaltene structure in crude oil is summarised in the Yen-Mullins model which classifies 'asphaltenes' as asphaltene molecules, nanoaggregates and clusters of nanoaggregates [5]. The asphaltenes present in processed crude oil such as HFO may have slightly different structures because of thermal or catalytic reactions [14]. More exact chemical data are required to relate structure to the thermal decomposition reactions [13,15] and cenosphere formation [16] during the combustion of heavy fuel oil.

Xu et al. [6] proposed average structures for bio-asphaltenes on the basis of methods employing NMR and infra-red (IR) spectroscopy originally developed for application to fossil-fuel asphaltenes. They put forward structures for bio-oil asphaltenes made up of a small number of approximately two ring polycyclic aromatic nuclei and oxygen-substituted saturated rings e.g. furans, and ketones, all linked together by 1–3 carbon alkyl groups. Nearly all of the rings and linking groups carried substituent aldehyde, alcohol, carboxylic acid, and phenolic hydroxyl and methoxyl groups. These structures differ from heavy-oil asphaltenes principally in that they contain fewer aromatic groups, and many more oxygen-containing rings and groups along with oxygen-containing substituents; the characteristic long-chain alkyl and methyl groups are absent, as are sulphur-containing aromatic groups. While such structures are useful indicators of the type of functional groups linked together, they do not take into account the distribution of structures about a mean.

Previously we investigated the influence of asphaltenes on the combustion of heavy oils by burning oil droplets with different asphaltene content either suspended singly, by passage through a drop tube furnace, and by spray combustion [13,15]. It was observed that asphaltenes reduced ignition delay because of the volatiles generated by pyrolysis The influence of asphaltenes on combustion did not affect droplet burning time; the stack solids collected during spray combustion depended in a second-order manner on the asphaltene content of the oil. The emitted smoke is made up of residual fuel, soot particles and cenospheres.

In this paper, we discuss and re-interpret in the light of the present work, the results from our previous experimental studies [13,15] of the rates of combustion of droplets, and hence sprays, of these fuels; the combustion mechanism; and the way in which fine particulate soot and cenospheres are produced. The significance of this information in relation to oil-fired boilers and to slow-speed Diesel engines is described and the influence of the chemical composition of the fuels, especially the asphaltenes, of the heavy fuel, and the analogous compounds present in the bio-fuel is discussed. The relationship between the devolatilisation of petroleum asphaltene and bio-asphaltene, the extent of their char formation and the rates at which they burn-out, are discussed.

We extend preliminary Py-GC–MS experiments [15] which gave results consistent with the thin-film pyrolysis results of Karimi et al. [11]. Here we employ complementary atomic emission detection (AED) which is a versatile highly selective detector for fossil-fuel derived materials analysed by GC (Py-GC-AED).

2. Experimental methods

2.1. Asphaltenes and their characterisation

Petroleum heavy oils with asphaltene content of 16 wt% were employed. *n*-Heptane insoluble asphaltenes were separated from a Marine Bunker C fuel oil and a Heavy Fuel Oil by a method consistent with ASTM method D2007-80 [15]. Bio-asphaltenes were separated from a fast pyrolysis pine-wood bio-oil as the fraction insoluble in *n*-heptane but soluble in toluene, a procedure consistent with the often applied solvent separation of bio-oil which yields a fraction insoluble in *n*-hexane and water, but soluble in dichloromethane.

The composition of the oil asphaltene used is similar to those studied previously by us [13,15]. The carbon content of the petroleum asphaltenes were 81.4–83.3 wt%, the sulphur content 1.7–3.0 wt%, nitrogen 1.2–1.5 wt%, vanadium 1750–1755 mg kg^{-1}, and a small amount of oxygen. In contrast the carbon content of the bio-asphaltene was 56.9%, oxygen 36.7 wt% and sulphur and nitrogen were both negligible.

2.2. Differential thermogravimetric analysis

This was carried out using a Stanton Redcroft DTA Instrument capable of undertaking thermogravimetric analysis (TGA) and the first derivative of the weight loss curve. 15 mg samples of the asphaltenes were first heated at 105 °C and then at a heating rate of 20 °C min^{-1} to determine the rate of volatiles loss and the amount of residual char formed. Air was then injected which oxidised the char leaving the residual ash.

2.3. Pyrolysis-GC–MS of asphaltenes

Py-GC–MS was carried out at known temperatures as described previously [15] with a 60 m long 0.25 μm film thickness column. The GC peaks were identified from the NIST library, from the literature, from the retention times of standards chromatographed under the same conditions.

For Py-GC-AED the MS was replaced via a transfer line, heated at 320 °C, to a JAS AED plus G2350A instrument set to measure the intensities of the emissions at the appropriate wavelengths. For detection of vanadium compounds the GC column was short (5 m) and coated with a thin (0.1 μm) film. Helium was the make-up gas at 40 mL min^{-1}. The AED utilised a high-purity (99.99%) helium microwave induced plasma (MIP) contained within a polyimide-coated silica tube and water-cooled to 63 °C. The spectrometer was purged with O_2-free nitrogen.

3. Experimental results

3.1. Thermal analysis of asphaltenes and bio-asphaltenes

TGA experiments were made of the asphaltenes from the two petroleum oils and the bio-oil. The mass loss plots are shown in Fig. 1(a) and the differential rates are shown in Fig. 1(b). They consist of three major parts: pyrolysis, decomposition of the asphaltene to form a char, and when the combustion air is admitted, the char burns off leaving any inorganic residue. The two petroleum asphaltenes have similar mass loss profiles and they have, as shown in Fig. 2 the same temperature at which the maximum loss rate occurs, namely at 484 °C. The experimental results here for the loss of the volatiles follow kinetic rates which are similar to those found in our previous studies [15] and by other research groups [17–19] as discussed later.