Article:

A Study of the Combustion Chemistry of Petroleum and Bio-Fuel Oil Asphaltenes

Farooq A. Atiku[1], Keith D Bartle[1], Jenny M. Jones[1], Amanda R. Lea-Langton[2] and Alan Williams[1]

1. Energy Research Institute, Leeds University. Leeds LS2 9JT, UK
2. Permanent address: MACE, Manchester University M13 9PL, UK

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.

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

1

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 1mm 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 of 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 16wt% 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 81.4-83.3wt%, 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 Thermal Analysis (DTA)

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 (DTA). 15mg 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.

2.2. Pyrolysis-GC-MS of asphaltenes

Py-GC-MS was carried out at known temperatures as described previously [15] with a 60m long 0.25µm 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 (5m) and coated with a thin (0.1µm) 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.

Bio-asphaltene behaves in a significantly different way in that pyrolysis of the bio-asphaltene occurs at a much lower temperature. Indeed the temperature at which the maximum pyrolysis rate occurs (234°C) is similar to that for the potassium catalysed decomposition of biomass (233°C) [20]. Potassium promotes the generation of phenol and phenol derivatives (2-methoxyphenol, 2,6-dimethoxyphenol) during biomass pyrolysis. Bio-oil is known to contain a range of complex oxygenated molecules [21] and the extraction process used here has separated out the bio-asphaltenes, many of which have chemical structures analogous to the biomass components [6] themselves. A detailed kinetic analysis of the decomposition was not undertaken here because of concerns about the reproducibility of the source material, the bio-oil.

-Fig. 1 here-

6

3.2 Py-GC-MS of fuel-oil asphaltenes.

A number of studies [eg 11,14,15, 22] have shown the evolution of a range of n-alkanes and monocyclic aromatic hydrocarbons at pyrolysis temperatures up to 400°C but by 600°C studies have shown [11,14,15, 22] that there are prominent peaks attributed to alkanes/alkenes indicating the commencement of secondary pyrolysis; these lower alkane/alkene pairs extended from C_{13} to C_{26}. This continued in the experiments reported here when the pyrolysis temperature was increased to 900°C (Fig 2a), but concentrations of low MW alkanes/alkenes decreased and was accompanied by some alkylated benzenes and, in smaller quantities, naphthalenes. At 1000°C however the alkanes beyond C_{10} were almost completely depleted (Fig. 2b) and ring fragmentation occurs and polynuclear fragments appear. Burning droplets would reach temperatures in this region.

-Fig. 2 here-

In addition to the alkanes and alkenes, the primary pyrolysis products of all of the asphaltenes detected by Py- GC –MS were C_1-C_4 alkyl substituted aromatic hydrocarbons, especially: benzenes; styrenes: methyl styrenes; naphthalenes and hydrogenated naphthalenes (dihydroindenes, dihydromethanonaphthalene and tetrahydronaphthalenes); phenanthrenes and anthracenes; pyrenes and isomers (fluoranthene and acephenanthrylene); and at high temperatures, traces of chrysenes. The classes of compounds identified are listed in Table 1, along with positions of methyl substitution when these could be identified. Naphthalenes and phenanthrenes with up to and including C_4 alkyl substitution were particularly prominent from 400°C to higher temperatures.

-Table 1 here-

No systematic change of composition within isomer groups with temperature was detected although as the pyrolysis temperature rose there was evidence of de-methylation; for example, the ratio of monomethylphenanthrenes to dimethylphenanthrenes increased, while

7

the degree of alkylation of naphthalenes was much less at the higher temperatures. The evolution of alkyl benzenes was significant from 500°C, and then released increasing quantities of at first C_4 benzenes followed by C_3 and C_2 benzenes as demethylation became important. Alkyl substitution in the dimethynaphthalenes from asphaltene pyrolysis favoured the 1-position.

AED detection revealed in Fig. 3 the presence of numerous polycyclic aromatic sulphur compounds (PASH) in the pyrolysis products, especially benzothiophens and dibenzothiophens with the latter predominant at 450°C; these relative intensities were reversed at 600°C. Sulphur isosteres of the PAH discussed above clearly contribute to the asphaltene structure. The pattern of alkyl group substitution on the benzothiophens and dibenzothiophens (Fig. 3) liberated from the asphaltene during Py-GC-AED, at least as far as C_3 derivatives, involved mainly methyl groups. The prominence of compounds with methyl at the 4- and 6- positions i.e. adjacent to sulphur, is noticeable, however; the same range of compounds identified by MS and literature retention data were shown by AED to be produced by pyrolysis at 450, 500 and 600°C.

-Fig. 3 here-

Because of poor selectivity arising from interference by lines in the carbon emission spectrum, the results of the Py-GC-AED with nitrogen detection (174 nm) show only poorly resolved 'background' of low-concentration nitrogen compounds. Seemingly only some of the nitrogen compounds present are volatile.

Relatively volatile vanadium compounds could be passed through a short thin-film SIMDIST capillary gas chromatographic column programmed to 350°C (Fig. 3): the vanadium compounds were detected by AED by atomic emission at 292 nm with simultaneous detection of carbon at 248nm.

3.2 Py-GC-MS of bio- asphaltenes.

It is seen from Fig. 1 that the behaviour of the bio-asphaltene is significantly different to the two petroleum-derived asphaltenes. The asphaltene separation process would be expected to extract the phenolic monomers and oligomers, leaving the sugars and water soluble compounds behind, and that the phenolic monomers would be relatively volatile. Py-GC-MS of the bio-aphaltene at 400°C is shown in Fig. 4 and at 800°C in Fig. 5.

-Fig. 4 and 5 here-

It is seen from that PAH with only up to two rings are liberated on pyrolysis at temperatures below 800°C when secondary reactions come into play; beginning at 400°C the products of pyrolysis are mainly C_1-C_3 benzenes and naphthalenes with some hydrogenated naphthalene structures (see Table 1), together indicative of an origin in phenylpropane and naphthenic structures in the bio-oil asphaltene molecules. There is competition between devolatilisation and char-forming reactions and the latter involve mainly the oxygen-containing (phenolic) parts of the asphaltene molecules.

4. Discussion

4.1 Thermal decomposition reactions of petroleum asphaltenes

The TGA curves for the fuel oils show that thermal decomposition consists of two major parts, initial pyrolysis together with loss of alkanes/alkenes and char forming reactions [15,16,23]. In these experiments air is then injected and it is followed by char burn-out. Both petroleum asphaltenes studied here are very similar in their behaviour.

The initial pyrolysis results from fission of the bonds linking the aromatic sub-units in the parent asphaltene from about 400°C with loss of volatile species. The global activation energies determined from this region are considerably smaller (91-105 kJmol^{-1}) than typical

bond-dissociation energies. This is in agreement with our earlier work but using a different HFO and the low values result from the parallel radical attack and sequential reaction paths and is consistent with other work with model compounds [18].

At the lower temperature, the long alkyl chains break off to yield a characteristic pattern of alkanes/alkenes. These alkane/alkene pairs of peaks in the pyrolysis products arise from alkyl radicals generated by beta-bond scission of long-chain alkyl aromatics. Evidence for this comes from, for example, the pyrolysis of n-pentadecylbenzene which gave rise to toluene and alkane/alkenes, and from dodecylbenzene which gave rise to undecene/undecane, toluene and ethylbenzene [24]. These peaks are still seen at 900$^{\text{o}}$C (Fig 2 a) although they much more prominent at lower temperatures such as 500$^{\text{o}}$C as previously shown [11,15,18], but by 1000$^{\text{o}}$C they are not so visible as the aromatic structures decompose (Fig. 2b).

At the higher temperature, the PAH structures decompose to yield 1-4 ring structures with alkyl substituents, thus giving a pattern of aromatic species similar to that observed in petroleum–based Diesel fuel. The aromatic products of pyrolysis of asphaltenes are indicative of a structure made up of linked aromatic clusters, termed 'building blocks' by Karimi et al. [11]. These are the conjoined small (1– 4) ring systems in Table 1. The fact that no polynuclear aromatics, even two-ring aromatic compounds, were produced by pyrolysis at 300$^{\text{o}}$C (as confirmed by TGA) indicates that bond breaking is necessary is necessary to bring about the release of PAH building blocks. It is possible that monocyclic aromatics produced at high temperatures originate in part from the pyrolysis of the aliphatic hydrocarbons. Indications of the nature of the structures linking the aromatic ring systems are provided by the identification of unsaturated naphthenic and hydroaromatic compounds in the asphaltene pyrolysis products. Furthermore, the high degree of methyl substitution of the naphthalenes and other aromatic units points to the breaking of alkyl bridges between building blocks. Some of these are the remnants of the loss of the long chains which can form alkanes which

are released into the gas phase and can act as ignition promoters, this is seen experimentally [15]. It must also be emphasised, however, that larger aromatic ring systems with six or more rings would not be eluted under the GC conditions employed here, so that the presence of large-aromatic asphaltene structures is not excluded; indeed these would play a role in char or cenosphere formation. TGA results are also consistent with the major weight loss at temperatures between 400-400ºC. There was little evidence for further weight loss at higher temperatures necessary to give rise to larger PAH species.

The relative proportions of alkyl benzothiophens and dibenzothiophens in the asphaltene Py-GC-AED products were determined from the corresponding AED peak areas using response factors per unit mass of sulphur determined for standard PASH (benzo[b]thiophen, dibenzothiophen, diphenylsulphide and diphenyldisulphide); these were always near unity. Alkylated DBT were liberated in the concentration sequence $C_2 > C_1 > C_3$ and exceeded the total alkylated BT in the ratio 2.1 to 1. It is proposed that sulphide bonds are broken and lost during pyrolysis along with other groups linking the aromatic/heterocyclic building blocks.

Knowledge of the identity of nitrogen-containing compounds liberated from asphaltenes during pyrolysis is important. The evidence here suggests that the nitrogen compounds, which are predominantly non-basic are not volatile and accumulate in the high molecular weight residue, that is, the char or cenosphere.

Vanadium is one of the most abundant metals in heavy oils and there is a roughly monotonic rise in its concentration with the asphaltene content of the oil. An exponential rise of concentration with residence time in drop-tube experiments [15] was observed indicating an association of the metal with the char or cenosphere formation and combustion and consistent with the observations of vanadium in the total particulate matter emissions. Some of the predominant alkyltetrapyrrole vanadium porphyrin structures (etio and deoxophylleoerythro (DPEP)) in which the metal is bonded are stable up to temperatures of

approximately 400°C and were shown by GC with selective AED to be volatile enough to pass into the gas phase from which smoke arises. As the temperature rises, any remaining vanadium porphyrins or metal compounds bound into the asphaltene structure decompose and accumulate in the char from which the cenospheres are formed. The volatile vanadium porphyrins meanwhile are available for the gas phase formation of soot components via routes analogous to those resulting in the formation of PAH.

4.2 Pyrolysis reactions of bio-asphaltenes

Asphaltenes are an empirical solubility class defined here as the fraction insoluble in an alkane but soluble in toluene. Poor solubility in an alkane is brought about by association of asphaltene molecules which are held together in the Snape-Bartle model [4] by interactions of either polyaromatic structures through pi-pi overlap, or of polar mainly phenolic groups which is most likely here. Reactive radicals resulting from the short residence time depolymerisation of the asphaltene oligomeric structures either abstract hydrogen to give readily ignitable low MW aromatics or cross link to form char. Pyrolysis of bio-asphaltenes with the structures proposed by Xu [6] might be expected to produce small alicyclic and aromatic molecules by first bond breaking of methoxyl groups followed by abstraction reactions to yield a multiplicity of oxygen-containing low molecular weight alicyclic compounds with aldehydes, carboxylic acids, phenols and phenolic oligomers as major constituents identified in bio-oil [21]. Some aromatics are also present. Two- ring and higher aromatic PAH can lead to soot via the HACA (hydrogen-abstraction-acetylene-addition) mechanism which is proposed in [15], while a carbonaceous residue forms from cross linking, especially of the hydrogen-donor bio-asphaltenes. In fact, pyrolysis products of the bio-oil asphaltenes at 400 and 800°C (Figs 4 and 5) contain mainly alkyl phenols and methoxyphenols. These are also similar to the primary products of biomass pyrolysis

[20,25,26]. At higher temperatures (e.g. 800°C, Fig. 5) secondary reactions lead to the elimination of oxygen and the formation of alkylated 1-3 ring aromatics [25,26]. These then form smoke since the cracking of alkyl phenols to CPD is an important route, or they go on to form chars. The amount of fixed carbon (char) produced by the bio-asphaltene is 20% compared with 58% from the Marine asphaltene and 48% from the heavy fuel oil. It is interesting to note that that although the maximum rate of decomposition occurs at 234°C the reaction continues until about 700°C when it levels off giving the maximum yield of char. This is the same temperature at which the petroleum asphaltene char formation ceases; this is indicative that the decomposition of the bio-asphaltene consists of two major routes, the decomposition of the oxygenated species and the char-forming reactions of the polyaromatics.

4.3 Combustion of petroleum derived oils.

The combustion mechanism of droplets in a spray involves the evaporation of parent oil species which are largely oxidised to CO_2 or form smoke, but some of the higher molecular weight species remain in the droplets at high temperatures and form a carbonaceous char or cenosphere. At the same time heavy oil N and S-compounds undergo decomposition forming volatile species which are oxidised to NO and SO_2 or form high molecular N/S species which remain in the cenospheres or char, these being released later as they are combusted. High molecular weight species are released later as the asphaltene undergoes thermal decomposition leading to condensed aromatic coke precursors by carbon rejection processes: de-alkylation and aromatisation (of respectively aromatic and hydroaromatic species), as well as oxidation.

During droplet combustion the large PAH species concentrate near the droplet surface forming a flexible carbonaceous skin which then forms a solid cenosphere containing blow

holes. However this process cannot occur during char formation in a TGA apparatus because the sample is contained in a small crucible so only a layer of char is formed.

A key issue is how this relates to the formation of soot and carbonaceous solids. It has previously been shown that the cenosphere content is about 90% of the total particulate matter emitted and that the amount of the stack solids vary with the half power of the asphaltene content and the half power of the flue gas oxygen content [15]. It has also been concluded that the major source of the cenospheres is the asphaltene content and that that the conversion efficiency of the asphaltene to stack solids is about 25%. Consequently it is possible to estimate the formation of stack solids in combustion chamber for a fuel with a known asphaltene content although allowance has to be made for the burnout of the carbonaceous material, as discussed later.

4.4 Combustion of bio-oils

Bio-oils consist of a range of oxygenated species together with some aromatic compounds with with some water and some water-soluble organic compounds [21]. Their burning rates are similar to those of petroleum based fuels [27,28]. Wornat et al. [27] in their study of single droplets of bio-oil found that combustion resulted in the formation of smoke and a small quantity of cenospheres. The bio-oil they used had a fixed carbon content of 15.5 wt % compared with the fixed carbon content of 20 wt% of the bio-asphaltene studied here. Studies have been made of bio-oils in commercial burners [29,30] and their emissions are similar to those from heavy fuel oils, with a range of particulate matter extending up to 10 µm. These bio-oils are known to contain aromatic structures eg [31] and so their behaviour is analogous to heavy fuel oils containing asphaltene.

4.5 Routes to particulate formation during heavy fuel oil and bio-oil combustion and its

   burn-out

In the case of the petroleum fuel oils the particulate emission consists of sub-micron soot and

cenospheres; both are increased by increasing the asphaltene content of the oil. Over 90% of

the cenospheres had diameters between 5 and 15 μm [15], and this is consistent with studies

using a commercial burner [1]. There is considerable variation in morphology; some are

larger with high ash content, but others were smaller and smooth with much lower ash

content. Surface area measurements show that the cenosphere skin thickness increases with

the asphaltene content of the oil since the surface area becomes smaller; for example, the

surface area of the cenospheres from the spray combustion of 3% asphaltene was 7.6 m^2g^{-1}

while that of the cenospheres from 6% asphaltene was 4.5 m^2g^{-1}. The fine soot results from

the reactions of the gas phase light aromatic species.

An analogous situation may hold for the bio-oils. That is, if each droplet produces a

cenosphere as is the case with the petroleum fuels, then the mass of stack solids would be

proportional to the bio-asphaltene content, although this is an untested hypothesis. Likewise

the yield of the gas phase soot would depend on the on the amount of volatile phenolic

species-although the oxygen content in the bio-oil will tend to mitigate cenosphere and soot

formation

   The burn-out rates of the cenospheres in the hot end of the combustion chamber determine

the amount of stack solids that are actually emitted. These can be calculated using the

intrinsic reaction rate, ρ_p, for the rate of oxidation of a carbonaceous material.

The rate (R) of burn-out is given by equation (1), where:

$$R = f (A_p, T_p, \rho_p, P_{ox}, k_{eff}) \tag{1}$$

and the rate is determined by the surface area of the particle, (A_p), the particle temperature

(T_p), the intrinsic reactivity of the particle (ρ_p), the partial pressure of the oxygen (P_{ox}) and the

effectiveness factor, k_{eff}. The latter is determined by the porosity of the char and is the ease in which oxygen can reach the reactive carbon surface; it is a very temperature dependent term but the value is close to unity towards the end of a combustion chamber.

The intrinsic reactivity of a wide range carbons have been determined by Smith [32] and the rates that he obtained are shown in Fig 6, which is based on reference [33]. The experimental values obtained by Hampartsoumian et al. [33] for the rate of burnout of heavy fuel oil cenospheres are shown in Fig 6.

-Fig. 6 here-

The burnout behaviour of the two petroleum asphaltene chars and the bio-asphaltene char are very similar, although the curve for the Heavy Fuel Oil has undergone a disruptive step; overall the combustion behaviour is similar to the Bunker C oil. It must be concluded that the presence of the vanadium in the petroleum fuel oils does not have a catalytic influence since the bio-asphaltene only contains trace amounts of metals. An alternative approach is to calculate the intrinsic reactivity. Taking the case of the Bunker C asphaltene it is necessary to know both the rate of char oxidation from Fig. 1 and the surface area of the char produced. Based on the values obtained previously [15] the surface area of cenospheres from a Heavy Fuel Oil containing 16wt% asphaltene is estimated to be 10 ± 2 m^2 g^{-1}. However in the measurements made here the sample is contained in a crucible resulting in the initial formation of a molten layer at the base which then forms a char layer. The surface area of this char layer is calculated on the basis that each particle is adjacent to its neighbour and the surface area is given by the summation of the hemispherical surface area of all the particles; this gives a value for the surface area in the range of the 1 to 2 m^2g^{-1}. On this basis the intrinsic reactivity was determined and this point obtained is shown in Fig 6; at 870°C the intrinsic char oxidation rate with an error of a factor of 2 is $1x10^{-7}$ gcm^{-2} s^{-1} at an oxygen pressure at 101 kPa. The similarity of the data to that of carbon compounds generally shown

by Smith [32] is clear; it should be noted that the activation energy obtained by Smith is 180 kJ mol^{-1}. It seems that the vanadium content has little catalytic effect possibly because of the way it is bound into the structure of the carbon. The data obtained by Fan et al [23] using oxidative TGA of petroleum fuel oil is also consistent with these results. For low temperatures they obtained a value of 100 kJmol^{-1} and for high temperatures values between 190-230 kJmol^{-1}. The equivalent processes here would be for devolatilisation (91-105 kJmol^{-1}) and char burn-out (180 kJmol^{-1}).

An appoximate value for the rate of burn-out (on a mass basis) of the bio-asphaltene char has also been obtained at the same temperature. This value is three times greater than that for the petroleum asphaltene char and would put it close to the Smith [32] line. The point has not been put on Fig. 6 because of the uncertainties, the surface area is assumed to the same as the petroleum char, the oxygen content is not known and there are uncertainties relating the source (the provinence) of the bio-oil and hence this char. This arises because bio-oils are unstable due to polymerisation and condensation reactions which take place during storage; this tend to increase the molecular sizes of alicyclic and aromatic clusters although without significant altering the functionalities present [34].

5. Conclusions

Thermal analysis together with Py-GC-MS detection of petroleum asphaltenes revealed the presence in the products of mono and hydroaromatic compounds and numerous alkylated PAH in addition to long-chain alkanes and alkenes. Py-GC with AED showed that alkylated (up to and beyond C_3) PASH benzothiophens and dibenzothiophens were also produced. However, most of the nitrogen is thought to remain in the char residue. These results are consistent with a structure for asphaltenes in which alkyl substituted small (1 to 4 ring) aromatic and sulphur heterocycic ring systems are linked by bridging groups. At pyrolysis temperatures below 400ºC the volatile vanadium compounds in the asphaltene are transferred

to the gas phase and hence to the combustion soot. At higher temperatures involatile vanadium porphyrins accumulate in the cenospheres.

A general reaction scheme for thermal reactions of asphaltenes accounts for ignition and soot formation in the gas phase and cenosphere formation in the solid phase, all via formation and reaction of 'building block' radicals in the liquid phase.

New information is provided on the analogous bio-asphaltenes and a potential route to the formation of cenospheres is given.

References

1. Linak WP, Miller CA, Wendt JOL. Fine particle emissions from residual fuel oil combustion: characterisation and mechanism of formation. Proc Combust Inst 2000; 28:2651–2658.
2. Corbett JJ, Lack DA, Winebrake JJ, Harder S, Silberman JA, Gold M. Arctic shipping emissions inventories and future scenarios. Atmos Chem Phys 2010;10:9689–9704.
3. Lack DA, Corbett J. Black carbon from ships: a review of the effects of ship speed, fuel quality and exhaust gas scrubbing. Atmos Chem Phys 2012; 12: 3985–4000, 2012

4. Snape CE, Bartle KD. Definition of fossil-fuel derived asphaltenes in terms of average structural parameters. Fuel 1984; 63: 883-887.

5.   Mullins OC, Sabbah H, Eyssautier JI, Pomerantz AE, Barré L et al. Advances in asphaltene science and the Yen−Mullins model. Energy Fuels 2012; 26: 3986−4003.

6. Xu Q, Zhang Z, Zhang S, Wang F, Yan, Y. Molecular structure models of asphaltene in crude and upgraded bio-oil. Chem Eng Technol 2014; 37: 1198–1204.

7. Hosseinnezhad S, Fini EH, Sharma BK, Bastid M, Kunware B. Physiochemical characterization of synthetic bio- oils produced from bio-mass: a sustainable source for construction bio-adhesives. RSC Adv. 2015; 5: 75519.

8. Li DD, Greenfield ML. High internal energies of proposed asphaltene structures. Energy Fuels 2011; 25: 3698-3705.

9. Herod AA, Bartle KD, Morgan TJ, Kandiyoti R. Analytical Methods for Characterizing High-Mass Complex Polydisperse Hydrocarbon Mixtures: An Overview. Chem Rev 2012; 112: 3892-3923.

10. Alshareef AH, Scherer A, Tan X, Azyat K, Stryker JM, Tykwinski RR, Gray MR. Formation of archipelago structures during thermal cracking implicates a chemical mechanism for the formation of petroleum asphaltenes. Energy Fuels 2011; 25: 2130–2136.

11. Karimi A, Qian K, Olmstead WN, Freund H, Yung C, Gray MR. Quantitative evidence for bridged structures in asphaltenes by thin film pyrolysis. Energy Fuels 2011; 25:3581–9.

12. Morgan TJ, Alvarez-Rodriguez P, George A, Herod AA, Kandiyoti R. Characterization of Maya Crude Oil Maltenes and Asphaltenes in Terms of Structural Parameters Calculated from Nuclear Magnetic Resonance (NMR) Spectroscopy and Laser Desorption-Mass Spectroscopy (LD-MS) Energy Fuels 2010; 24: 3977-3989.

13. Waller PR, Williams A, Bartle KD. The structural nature and solubility of residual fuel oil fractions. Fuel 1989; 68: 520-526.

14. AlHumaidan FS, Hauser A, Rana MS, Lababidi HMS, Behbehani M. Changes in asphaltene structure during thermal cracking of residual oils: XRD study. Fuel 2015; 150: 558–564.

15. Bartle KD, Jones JM, Lea–Langton AR, Pourkashanian M, Ross AB, Thillaimuthu JS, Waller PR, Williams A. The combustion of droplets of high-asphaltene heavy oils. Fuel 2013; 103: 835-842.

16. Reddy VM, Rahman MM, Gandi AN, Elbaz AM, Schrecengost RA, Roberts WL. Cenosphere formation from heavy fuel oil: a numerical analysis accounting for the balance between porous shells and internal pressure. Combust Theor Model 2016; 20: 154-177.

17. Ambalae A, Mahinpey N, Freitag N. Thermogravimetric studies on pyrolysis and combustion behavior of a heavy oil and its asphaltenes. Energy Fuels 2006; 20: 560-565.

18. Alshareef AH, Azyat K, Tykwinski RR, Gray MR. Measurement of cracking kinetics of pure model compounds by thermogravimetric analysis. Energy Fuels 2010; 24: 3998–4004.

19. Alvarez E, Marroquín G, Trejo F, Centeno G, Ancheyta J, Díaz JAI. Pyrolysis kinetics of atmospheric residue and its SARA fractions. Fuel 2011; 90: 3602–3607.

20. Nowakowski DJ, Jones JM, Brydson RMD, Ross AB. Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice. Fuel 2007; 86:2389-2402.

21. Stas M, Kubicka D, Chudoba J, Pospisil M. Overview of analytical methods used for chemical characterization of pyrolysis bio-oil. Energy Fuels 2014; 28: 385-402.

22. Sarmah MK, Borthakur A, Dutta A. Pyrolysis of petroleum asphaltenes from different geological origins and use of methylnaphthalenes and methylphenanthrenes as maturity indicators. Bull. Material Sci. 2010: 33: 509-515.

23. Fan C, Zan C, Zhang Q, Ma D, Chu Y, Jiang H, Shi L, Wei F. The oxidation of heavy oil: thermogravimetric analysis and non-isothermal kinetics using the distributed activation energy model. Fuel Proc Tech 2014; 119: 146–150.

24. Behar F, Lorent F, Budzinski H, Desavir E. Thermal stability of alkylaromatics in natural systems: kinetics of the decomposition of dodecylbenzene. Energy Fuels 2002; 16: 831-841.

25. Evans RJ, Milne TA. Molecular characterization of the pyrolysis of biomass. 1 Fundamentals. Energy Fuels 1987; 1: 123–137.

26. Dufour A, Girods P, Masson E, Normand S, Rogaume Y, Zoulalian A. Comparison of two methods of measuring wood pyrolysis tar, J. Chromatogr. A 2007; 1164: 240–247.

27. Wornat MJ, Porter BG, Yang NYC. Single droplet combustion of biomass pyrolysis oils. Energy Fuels 1994; 8:1131–42.

28. Bartle KD, Fitzpatrick EM, Jones JM, Kubacki ML, Plant R, Pourkashanian M, Ross AB, Williams A. The combustion of droplets of liquid fuels and biomass particles. Fuel 2011; 90: 1113–1119.

29. Lehto J, Oasmaa A, Solantausta Y, Kyto M, Chiaramonti D. Review of fuel quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass. Applied Energy 2014; 116: 178-190.

30. Feng C, Gao X, Wu H. Particulate matter emission from bio-oil incomplete combustion relevant to stationary applications. Fuel 2016; 171: 143-150.

31. Wang Y, Li X, Mourant D, Gunawan R, Zhang S, Li C-Z. Formation of aromatic structures during the pyrolysis of bio-oil. Energy Fuels 2012; 26: 241-247.

32. Smith, IW. The combustion rates of coal chars: a review, Proc. Combust. Inst., 1982, 19, 1045-1065.

33. Hampartsoumian E, Pourkashanian M, Williams A. J. Inst. E. Combustion rates of chars of carbonaceous residues. 1989; 450: 48-56.

34. Cordella M, Berrueco C, Santarelli F, Paterson N, Kandiyoti R, Millan M. Yields and ageing of the liquids obtained by slow pyrolysis of sorghum, switchgrass and corn stalks. J. Anal Appl Pyrol 2013; 104, 316–324.

Table 1. Aromatic hydrocarbons identified in pyrolysis products of petroleum asphaltenes and bio-asphaltene.

	Petroleum asphaltenes	Bio-asphaltene
Benzenes[a]	Et. 1,2- Me_2. 1,3-Me_2. 1,4-Me_2 (106); 1,3,5-Me_3 1-Me-3-Et 1-Me-4-Et 1-Me-2-Et 1,2,4-Me_3 1,2,3-Me_3 (120); C_4 (134)	Parent (78), C_1-C_3 benzenes
Styrenes	Parent (104); Me (118); C_2 (132)	
Naphthalenes[a]	Parent (128); 1-Me 2-Me (142); 1,3- Me_2 1,6-Me_2 1,7-Me_2 (156); C_3 (170)	C_2-C_3 naphthalenes at $300 - 900^oC$
Phenanthrene[a]	Parent (178); 1-Me 2-Me 3-Me 9-Me(192); C_2 (206); C_3 (220); C_4 (234)	C_1-C_3 phenanthrenes (800-900^oC)
Anthracene	Parent (178)	
Fluoranthene	Parent (202)	
Acephenanthrylene	Parent (202)	
Pyrenes[a]	Parent (202) 1-Me 2-Me 4-Me (216)[b]	Parent (800-900^oC)
Chrysenes	Parent (228) 1-Me 2-Me 3-Me 6-Me (242)	

(a)

(b)
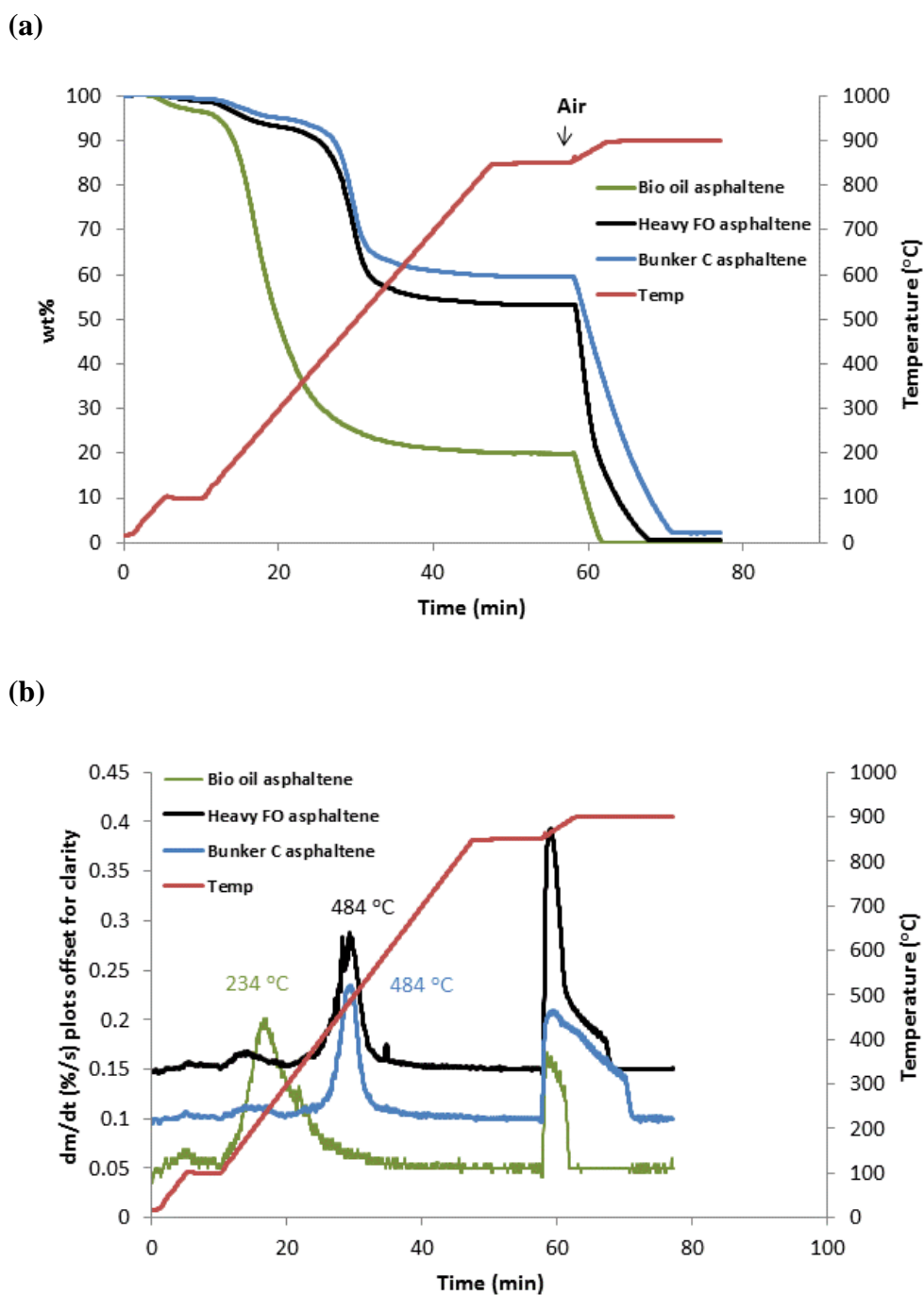
Fig. 1. Thermal Gravimetric Analysis showing (a) the weight loss and the temperature against time for Heavy Fuel Oil asphaltene, Bunker C asphaltene and bio-asphaltene (b) derivatives of mass loss (DTG) curves and temperature against time for the samples.
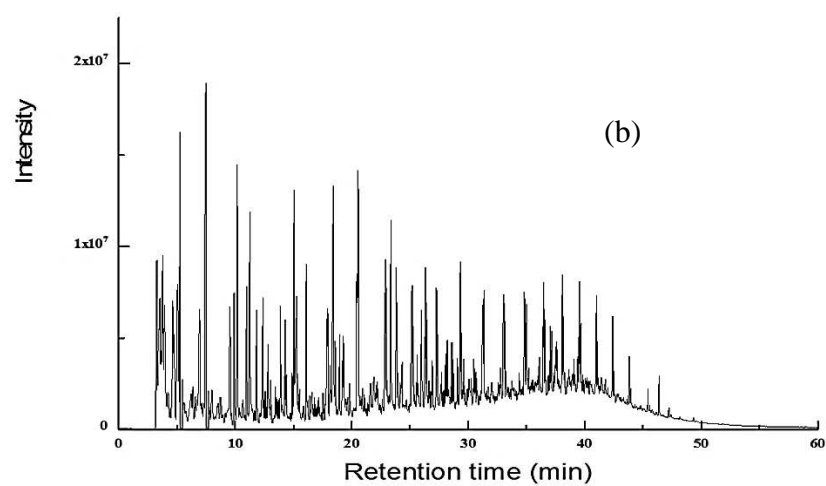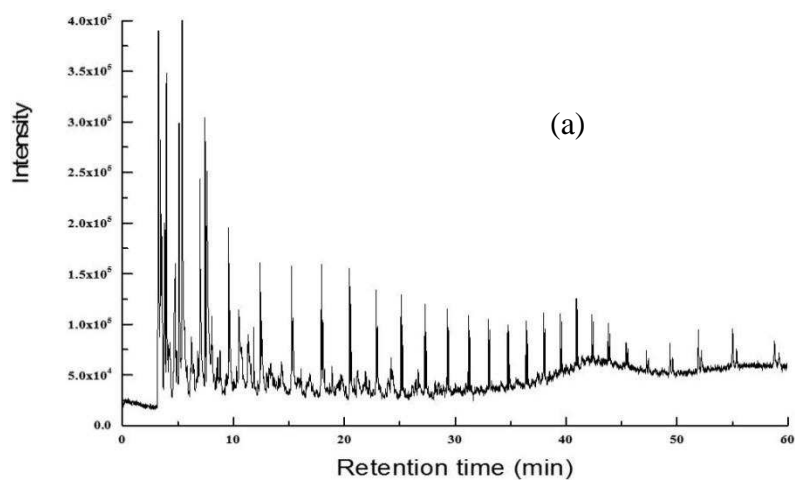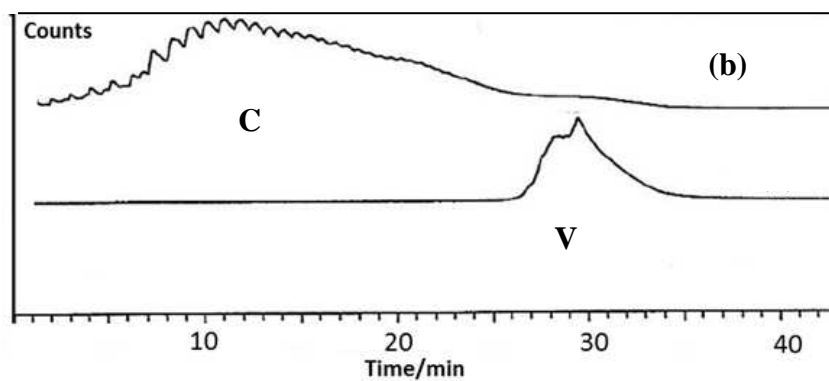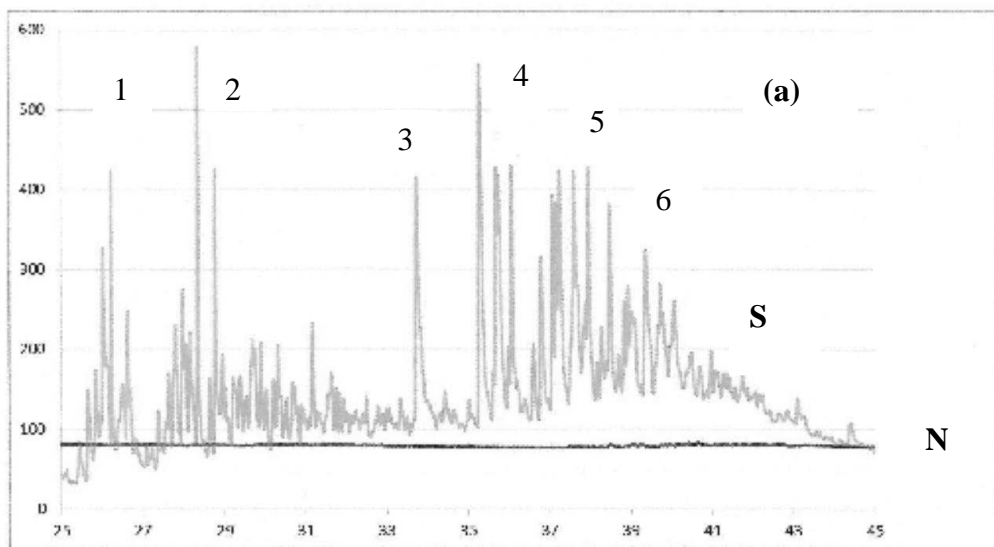
Fig. 2. Py -GC-MS of Heavy Fuel Oil asphaltenes at (a) 900 and (b) 1000°C. For conditions and peak identifications see text.

Fig 3. (a) Py-GC AED of Bunker C oil asphaltene with sulphur detection at 181nm (S) and nitrogen detection at 174nm (N), (b) High temperature gas chromatogram of Heavy Fuel oil with AED detection at 248 nm for carbon (C) and vanadium detection at 292nm (V).
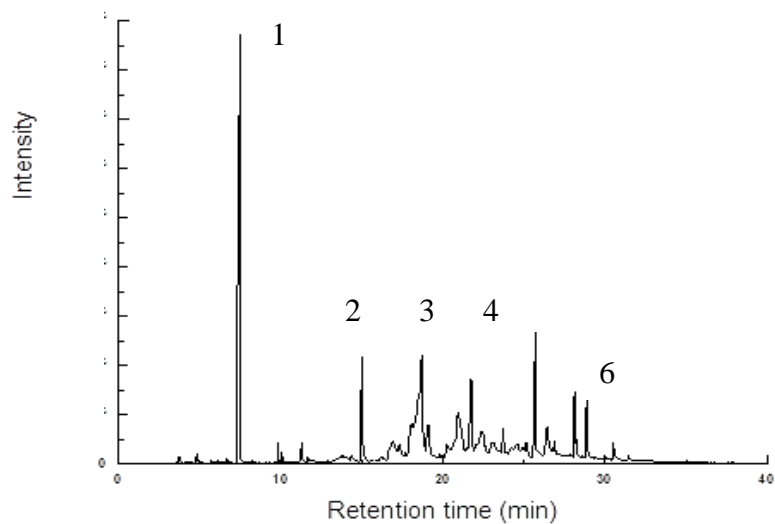
Fig 4. Py-GC-MS chromatogram of bio-oil asphaltene at 400°C. For conditions see text.

Species are: 1: toluene; 2: to be identified; 3: benzaldehyde; 4: 2-methoxy-4-(2-

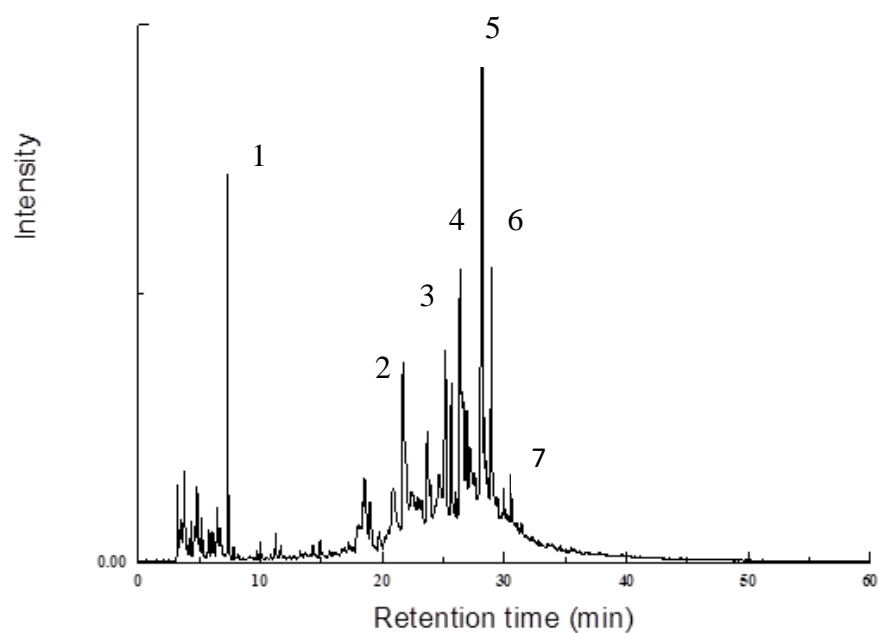propenyl)phenolacetate; 5: 2-methoxy-3-(2-propenyl)phenol, 6: vanillin.

Fig 5. Py-GCMS chromatogram of bio-asphaltene at 800ºC. Species are: 1: toluene; 2: 2-methoxy-4-methyl-phenol; 3: 2-methoxy-4-vinylphenol; 4: 2-methoxy-1,3-benzodioxole; 5: 2-methoxy-4-(2-propenyl)-phenolacetate; 6: 3-methoxy-4-(acetyloxy)-benzaldehyde; 7: 2-(1,1-dimethylethyl)-1,4-benzenediol.
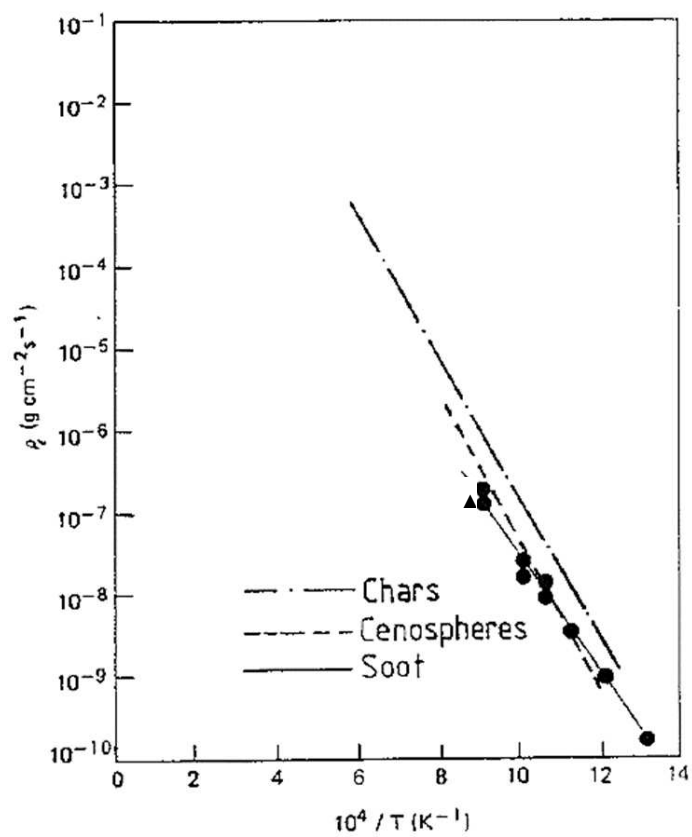
Fig. 6. Intrinsic oxidation rate of: chars and carbons; Smith [30], Heavy Fuel Oil cenospheres [31] and ▲, experimental point derived from Fig.1(a) for petroleum asphaltene. Oxygen pressure at 101 kPa.