SIZING AND CHARACTERIZATION OF PARTICULATE EMISSIONS FROM HEAVY FUEL OIL SPRAY COMBUSTION

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Abstract

Chemical and spectroscopic characterization of fine particles fraction (< 1 μ m) collected in the last stage (backup filter) of an *Andersen* impactor has been performed in flame and at the exhaust of a 100 kW spray burner burning heavy fuel oils having a different content of asphaltenes and aromatics.

The fine particulate was extracted in dichloromethane (DCM) for the analysis of soluble organic material by gaschromatography-mass spectrometry (GC-MS), size exclusion chromatography (SEC) and UV-visible absorption and fluorescence. The residual particulate material insoluble in DCM was treated in a very polar and powerful solvent as N-methyl-pyrrolidone (NMP) that is able to dissolve and/or to get stable suspensions of soot, allowing their analysis by means of techniques generally applied only on liquid samples, as SEC and UV-visible absorption and fluorescence spectroscopy.

SEC technique has allowed to evaluate a distribution of molecular masses and UV-visible absorption and fluorescence spectroscopy applied on DCM and NMP solutions of samples allowed to investigate similarities and differences in the chemical structure and in particular on the aromaticity of the particulate materials collected in the smallest dimensional ranges ($< 1 \mu m$).

Introduction

Many industrial processes and production energy systems are based on the combustion of heavy fuel oils that is an important emission source of particulates. This is due to the high content of metallic and heavy aromatic species which are known to enhance formation of inorganic and carbonaceous particulates, respectively. It is assessed that these particles produce significant effects on human health even at very low concentration [1] and that the size and/or the chemical composition of particles are very important in the production of damage [2, 3]. Heavy fuel oils are known to be prone to form both small soot particles and large size particulates ($\cong 100 \ \mu m$) named cenospheres whose formation is related to the asphaltene content in the heavy fuel oil [4-6]. Nevertheless, the existing information about the size distribution and the chemical composition of the particles originated by organic and inorganic compounds present into the fuel is still not adequate.

In a previous work [7] sizing in the 0-20 μ m range of particulate has been performed in a 100 kW spray burner by using an 8-stages *Andersen* impactor and samples from all stages were analyzed by scanning electron microscopy (SEM) equipped with an Energy Dispersive X-ray (EDX) spectrometer in order to have morphological information and elemental analysis of individual particles.

The present work is focused on chemical and spectroscopic characterization of fine particles fraction (< 1 μ m) collected in flame and at the exhaust of the same spray burner burning heavy fuel oils having a different content of asphaltenes and aromatics.

The fine particulate (< 1μ m) collected on the last stage of the *Andersen* impactor (backup filter) was extracted by means of ultrasonic agitation in dichloromethane (DCM) for the analysis of soluble organic material by gas-chromatography-mass spectrometry (GC-MS), size exclusion chromatography (SEC) and UV-visible absorption and fluorescence. The residual particulate material insoluble in DCM was treated in a very polar and powerful solvent as N-methyl-pyrrolidone (NMP) that is able to dissolve and/or to get stable suspensions of soot [8], allowing their analysis by means of techniques generally applied only on liquid samples, as SEC and UV-visible absorption and fluorescence spectroscopy.

SEC technique has allowed to evaluate a distribution of molecular masses and UV-visible absorption and fluorescence spectroscopy applied on DCM and NMP solutions of samples allowed to investigate similarities and differences in the chemical structure and in particular on the aromaticity of the particulate materials collected in the smallest dimensional ranges (< 1μ m).

Experimental set-up

Experiments were performed under controlled conditions in a 100 kW three-flux low NOX burner inserted in a vertical ceramic fiber furnace described in a previous paper [9, 11]. This furnace is equipped with optical and sampling accesses. The fuels were atomized by a commercial mechanical nozzle (full cone) keeping constant the fuel flow rate at 4.5 l/h, air excess at 20 % and a preheat air temperature of 100°C.

Isokinetic sampling was performed in flame and at the exhausts of the heavy oil spray flames under the same atomization conditions and the samples were size-segregated by means of an 8-stages *Andersen* impactor. This impactor is designed to collect samples on nine stages (including the backup filter) ranging between 0.5 and 20 µm in diameter for subsequent gravimetric and SEM and EDX analysis. Three data sets were taken for each experimental condition. Moreover, because of the too small existing stack, the sampling nozzle was extended to allow external isokinetic sampling. To accomplish that, the entire impactor and sampling nozzle were heated to avoid cooling down of the sampled gas. Samples were also analyzed by a SEM equipped with an Energy Dispersive X-ray (EDX) spectrometer. This provided morphological information about individual particles.

Two different heavy oils, named # 5 and # 6 on the basis of ASTM classification, were studied. The preheating oil temperature has been kept at 110°C and 145°C for # 5 oil and # 6 oil respectively, in order to obtain the same viscosity and hence the same droplet size during atomization. These oils have different asphaltene and metals content: # 5 oil only contains 1 % wt of asphaltene and 41.28 ppm of metals while # 6 oil contains 8 % wt of asphaltene and 100.7 ppm of metals.

Samples extraction: The backup filters from flame and exhaust sampling were extracted in dichloromethane (DCM) in an ultrasonic bath for thirty minutes, in order to separate the DCM soluble organic material from organic and inorganic particulate. After drying, filters were subjected to N-methyl-2-pyrrolidinone extraction in an ultrasonic bath for forty-five minutes to "dissolve" the organic particulate.

Size Exclusion Chromatography: Size exclusion chromatography was carried out on a HP1050 High Pressure Liquid Chromatograph equipped with an uv-visible Diode Array Detector detecting the absorption signals at 265 nm, 280nm, 350nm, 450 nm and 500 nm. The analyses were performed on a PLgel 5 μ m 500 Å column (highly cross-linked Polystyrene/divinyl benzene matrix) 30cm*7.5mm o.d. at a temperature of 80°C and an eluent flow rate of 0.5 ml min⁻¹. The solvent used to dissolve the samples and as eluent was N-methyl-2-pyrrolidinone (NMP).

The attribution of a molecular weight to a specific SEC retention time was made on the basis of a calibration curve using polystyrene standards in a very large molecular range (580-2,000,000 u), as better described in a previous work [10]. The logarithm of molecular weight versus elution volume gave a straight line over this molecular weight range. The upper mass limit (exclusion limit) is 2,000,000 u in terms of polystyrene standards.

UV-visible absorption spectroscopy: UV-visible spectra of the samples dissolved in DCM and in NMP were measured on an HP 84523 Diode Array spectrophotometer connected to a personal computer using 1-cm quartz cuvettes.

Fluorescence spectroscopy: Emission and synchronous fluorescence spectra of the samples were measured on a Perkin-Elmer LS-50 spectrofluorimeter connected to a personal computer.

Gas Chromatography-Mass Spectrometry (GC-MS): Polycyclic aromatic hydrocarbons up to 300u (GC-PAH) in the DCM extracts were quantified by gas chromatography-mass spectrometry (GC-MS) on an HP5890 gas-chromatograph, coupled with a HP5989A mass spectrometer, on a HP-5MS Crosslinked 5% PhMe Siloxane 30m length, 0.25mm i.d., 0.25mm film thickness column.

Results and discussion

The gravimetric determination of particulate material collected on filters from each stage of *Andersen* impactor sampling allowed to determine the particulate distribution functions at the exhaust of a # 5 oil and a # 6 oil spray flame and, for comparison, in the # 6 oil flame at 450 mm of height above the burner. Sampling at heights lower than 450 mm was not possible by means of an *Andersen* impactor as the flame temperature was too high (1600-1700 K) even utilizing glass fiber filters ($T_{max} = 700$ K).

As the formation of particulate is strongly related to the asphaltene content of the parent oil [4 - 6], # 5 and # 6 oils having different asphaltene level have been chosen to study asphaltene effect on the formation of particulates in terms of size and number density.

The particulate distribution functions of the sampled material are reported in Table 1.

As expected, #6 oil produces more particulate than the lowest asphaltene containing oil, #5, in each dimensional stage. The particulate concentration inside #6 oil flame is much larger than at the exhaust and this is particularly evident in the smallest dimensional fraction (< 1 μ m).

Stage	Diameter range size (µm)	# 5 oil exhaust (mg/Nm ³)	# 6 oil exhaust (mg/Nm ³)	# 6 oil flame (mg/Nm ³)
0	> 13.87	0.053191	0.5	1.503759
1	8.70-13.87	0	0.021739	1.353383
2	5.87-8.70	0.12766	0.326087	1.052632
3	4.04-5.87	0.085106	0.641304	0.601504
4	2.54-4.04	0.297872	1.413043	2.255639
5	1.38-2.54	0.180851	1.043478	1.203008
6	0.80-1.31	0.12766	0.336957	1.954887
7	0.55-0.80	0.074468	0.097826	1.503759
Backup filter	0-0.55	2.925532	7.88913	56.2406

Table 1. Particulate concentration in each dimensional stage.

After the weighing operation, further investigation was performed on the samples using electronic microscopy (SEM) coupled with X-ray analysis (EDX). As found in previous work [7], the most interesting result from these analyses was the detection of small full/solid particles, called plerospheres, whose composition was directly correlated to their dimensions. The smaller were the particles, the greater was their metallic content, while this metallic concentration resulted to be independent of the asphaltene content of the parent oil. However, the analysis was limited to the samples in the 1-20 μ m range whereas in the present work the characterization has been applied to the fine particulate (< 1 μ m) collected on the backup filters. The characterization of fine particulate is, indeed, becoming more and more important as recent study has shown growing evidence that smaller size particles induce stronger health effects in human beings than bigger particles [2-3].

GC-MS analysis of DCM extracts of backup filters revealed the presence of combustion-formed PAH mainly in the 128-202 u molecular mass range, with the prevalence of naphthalene (128 u) and fluorene (166 u). Fluorescence spectroscopy measured in the UV-visible range, which is characteristic of light aromatic emission, confirmed the predominance of light PAH and the almost complete absence of other heavier aromatic species. SEC analysis confirmed the presence of light PAH and only a negligible amount of higher molecular mass material (about 400-500u and 1000-2000 u) was detected.

Height normalized absorption spectra of #6 oil exhaust and flame NMP particulates are reported in fig.1 along with the spectrum of parent oil in NMP solution. The structureless feature of spectra indicates the absence of combustion-formed PAH that usually give fine structure spectra.



Figure 1. Height normalized absorption spectra of NMP samples from # 6 oil and of parent oil

The spectrum of the fine particulate sample collected in the exhaust is very similar to the parent oil one in the UV range (up to 350 nm), but in the visible a broad signal extending up to 550 nm appears, testifying the presence of heavy aromatic structures absorbing in the visible. Moreover, these structures are not fluorescing at all in UV-visible range both using a fixed excitation wavelength in UV and in the visible range and also acquiring a synchronous fluorescence spectrum (correspondent to continuous scan of excitation and emission wavelengths which are constantly separated by a wavelength differential empirically determined [12]).

In the case of flame NMP extract the similarity with parent oil is restricted to the region up to 310 nm, afterwards there is a change in the slope indicating the beginning of a broad absorption extending up to 500 nm.

The difference in the position of the broad bands in flame and exhaust sample indicates a different structure of the aromatic material in the two samples. In order to investigate if the difference was in the molecular weight (MW) distribution of the samples a SEC analysis was performed and the chromatograms obtained are reported in fig 2.



Figure 2. Height normalized chromatograms of NMP samples from # 5 and # 6 oils.

The SEC chromatogram of the flame sample presents a main peak at a lower molecular weight (about 2500 u) than the exhaust sample (about 4000u). Moreover, the main peak of the exhaust sample present a shoulder at 8000 u that is absent in the flame sample and this testifies that the shift toward the visible of the absorption signal is due to the presence of heavier structures. Both flame and exhaust samples present a SEC peak at 9 min of elution time (fig.2) that is out of the linearity range of SEC column and therefore corresponds to a molecular weight larger than 2,000,000 u.

The flame and exhaust samples chromatograms are compared in fig.3 with chromatograms of parent oil and of a typical soot sampled in flame in the soot formation region. It can be noted that the molecular range of the main peak of NMP samples (2500-4000 u) is completely absent in parent oil and soot. This indicates that the carbonaceous material mainly present in the smallest dimensional stage of *Andersen* impactor is constituted by flame-formed aromatic macromolecules not yet transformed in soot. This assessment seems to be supported also by the overlap between the small peak at 9 min of NMP samples and the main peak of the soot chromatogram (fig.3) that could indicate the beginning of a molecular growth up to MW typical of soot particles.

As regards #5 oil, the absorption spectrum of NMP exhaust sample is reported in fig. 4 along with parent oil spectrum. In analogy with #6 oil samples, we can observe a similarity with parent oil spectrum in the UV region whereas two broad signals at 330 nm and 450 nm can be observed not present in the fuel oil spectrum. SEC chromatogram of #5 oil exhaust sample reported in fig. 2 testifies that also in this case the material, which is absorbing in uv-visible range but not fluorescing, has a molecular weight of thousands of mass units (about 7500 u). Once more, the structure is due to a flame-formed material, since it is very different spectroscopically and in MW distribution from parent oil (this last comparison is not shown here), but it is also different from soot. It is not well understood why the MW of #5 exhaust main peak is larger than #6 oil flame and exhaust main peaks,

but it is evident that globally their structures are very similar: all are not fluorescing but absorbing in the UVvisible range testifying the presence of an aromatic structure probably too heavy for fluorescing, and all have MW lower than mature soot particles and could constitute soot precursors. The difference in the MW between flame and exhaust extract from the same fuel is probably due to the fact that these macromolecules grow along the flame and so they arrive with larger dimensions at the exhaust.



Figure 3. Height normalized chromatograms of NMP samples from # 6 oils, parent oil and soot.



Figure 4. Height normalized absorption of NMP sample from # 5 oil and parent oil.

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