20th ETH Conference on Combustion Generated Nanoparticles

Heteroatomic Nanostructures of Jet Fuel Soluble Macromolecular Oxidatively Reactive Species (SMORS)

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INTRODUCTION

- Thermal oxidative instabilities result in jet fuel degradation through deposition as a result of heating and oxidation which is harmful for aircraft gas turbine engine
- SMORS are deposit precursors and elementary heteroatomic units containing unsaturated and aromatic hydrocarbons. O, N and S containing compounds are present in trace amounts in jet fuel which as a result of primarily oxidation such as free radical reactions form nano and micron size solid particles
- Quinones, pyrroles, polynuclear aromatic hydrocarbons (PAHs) and phenols are few heteroatomic fuel components present in trace levels
- Objective of this study is to investigate both qualitatively and quantitatively SMORS and deposit formation as a result of thermal stressing of jet fuel
- Jet A is thermally stressed by 6 hours flask static tests at 190 ^{0}C followed by spectroscopic and microscopic analysis

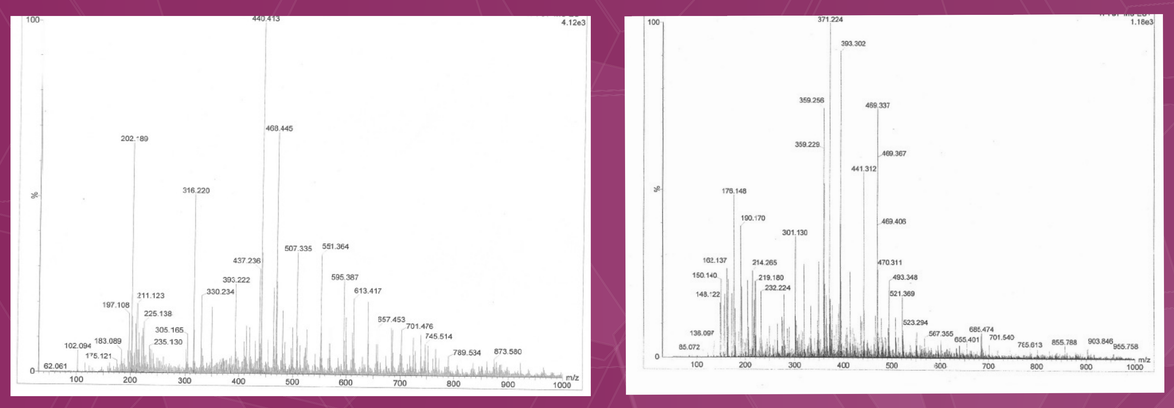

Figure 1: Mass spectra of Jet A thermally stressed samples extracted with methanol showing SMORS in the mass range >300 Da.

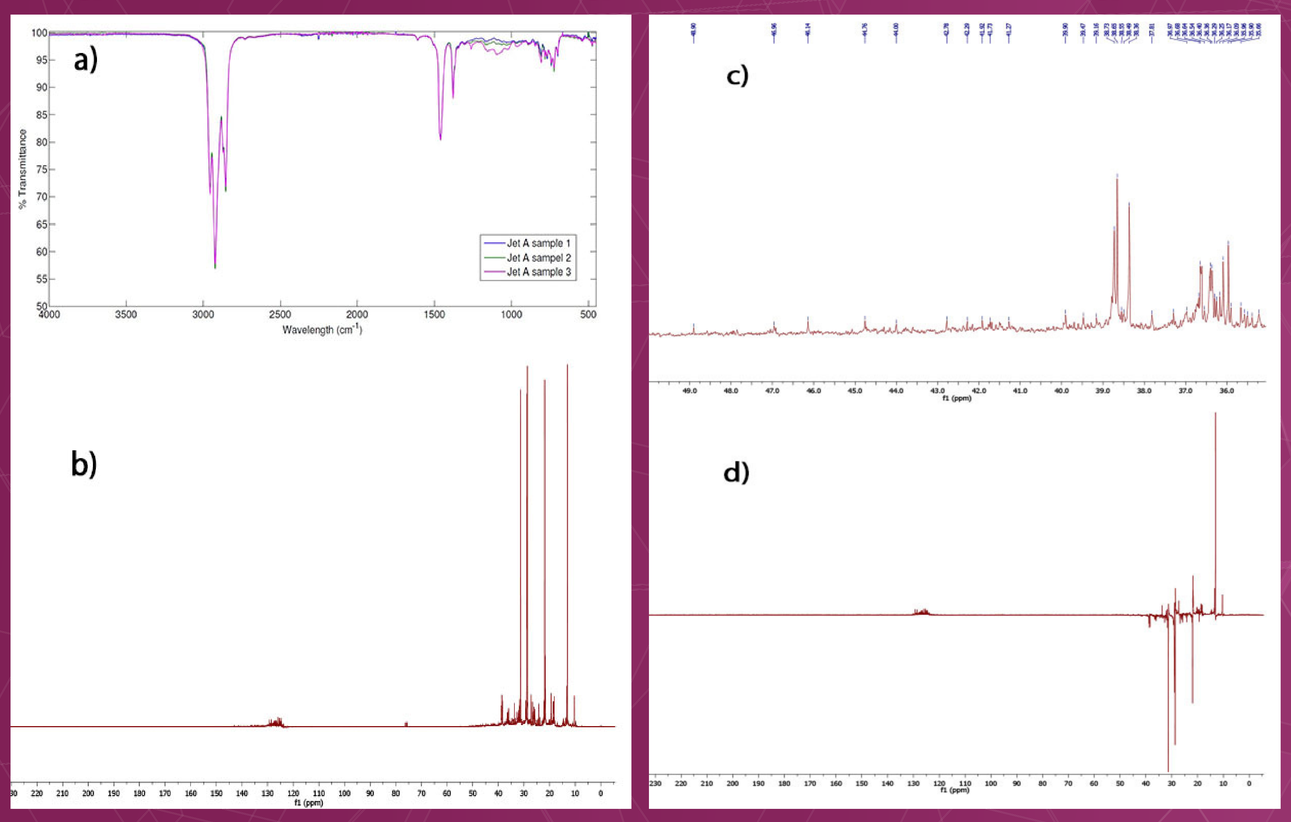

Figure 2: FTIR and 13C NMR spectra of Jet A; a) FTIR spectra showing additional peaks in the Jet A sample 3 in the 1000 to 1200 cm^{-1} , b) and c) NMR spectra of thermally stressed Jet A sample with peaks 35- 50 ppm indicating oxygen containing fuel components. And d) DEPT 135 showing CH_2 as inverted peaks.

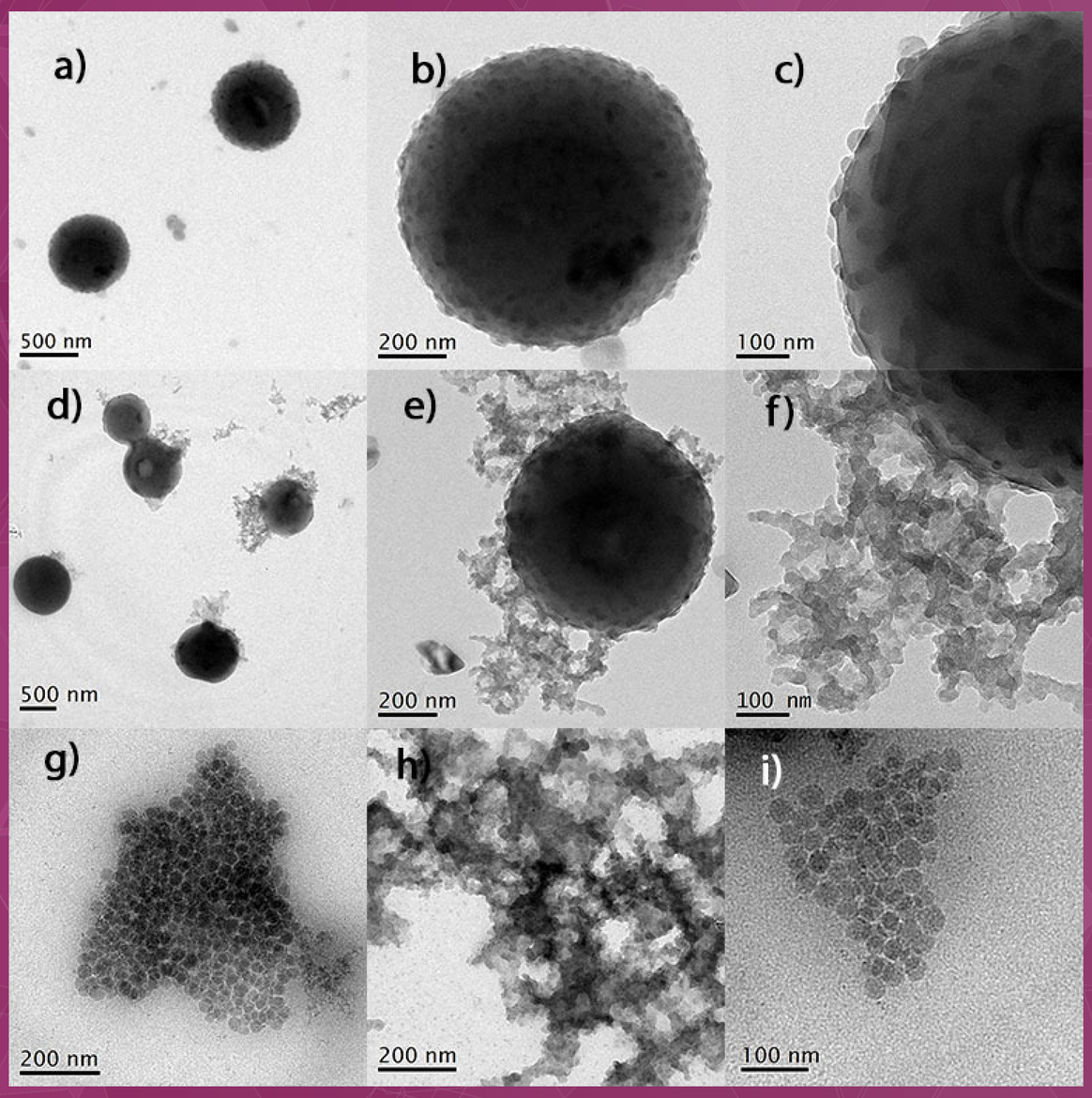

Figure 3: TEM images of Jet A SMORS and deposits nanostructures and their micron size agglomerates: a), b) and c) showing spherical micron size structures with elementary nanoparticles visible on the surface; d), e) and f) with micron size spheres connected with elementary nanostructures and g) to i) show nanostructures

RESULTS

- SMORS are recorded in the mass spectra of Jet A in mass range 300-1000 Da
- FTIR and NMR spectra reveal alkoxy species
- Uniquely, deposits nanoparticles and their agglomerates are spherical as shown in TEM and SEM images
- Nanostructures are in the range 10-80 nm, which can be broadly classified into two groups, first) 10- 30 nm and second) 40-80 nm. Nanoparticles upto 30 nm are relatively more than larger ones, however measurements are required to understand size distribution

In progress and future research

- Flask tests and fuel thermal stressing in the flow reactor with varying heating time followed by chemical analysis
- Quantitative measurements of thermally stressed fuel deposits
- LC-NMR analysis of SMORS
- Investigating (alternative) reaction mechanisms of SMORS and their agglomerates formation

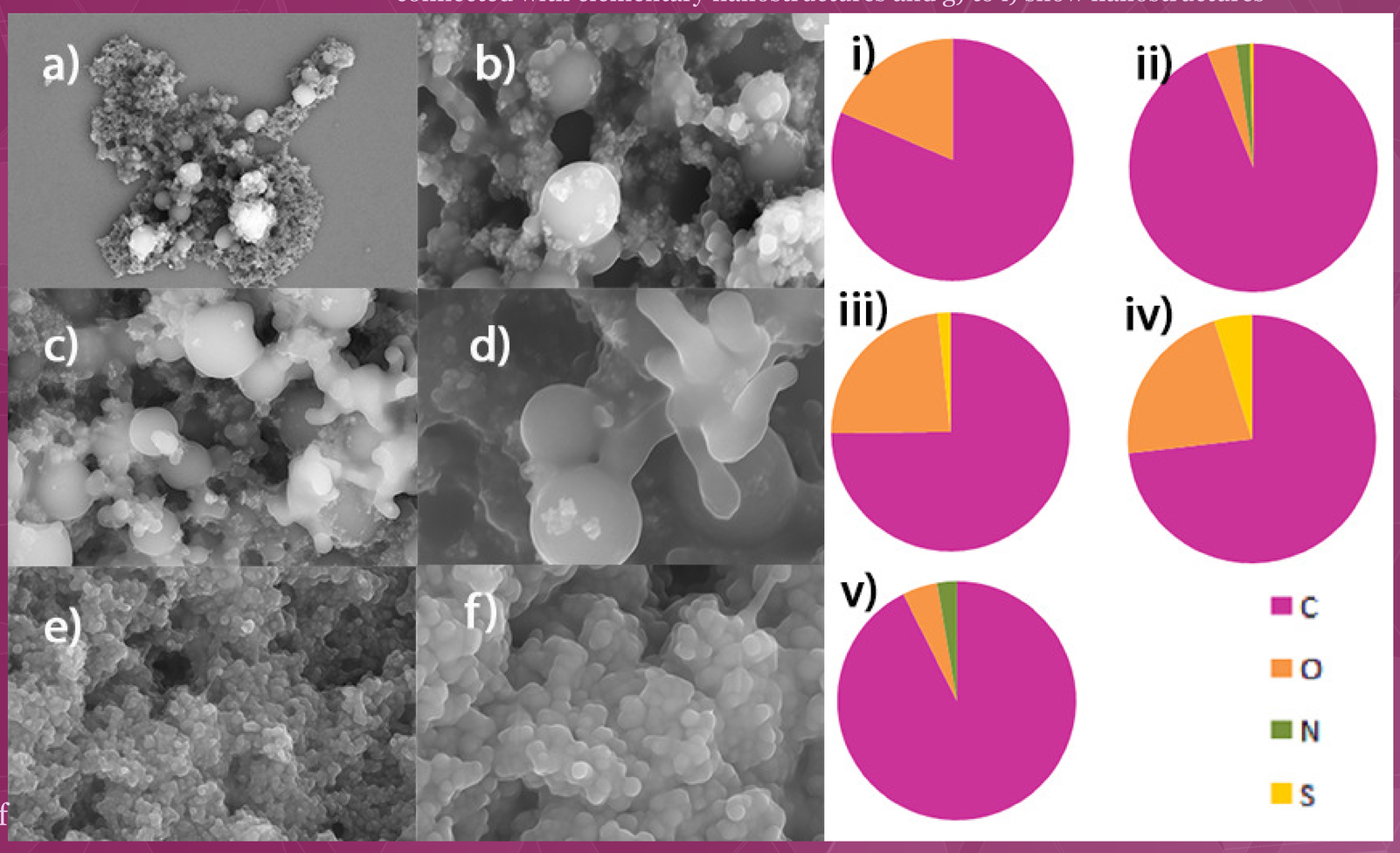

Figure 4: SEM-EDS images of Jet A SMORS and deposits nanostructures; a) and b) contain O and S as shown in i) and iii), SEM images c) and d) showing nanoparticles and agglomerates with C, O and S as shown in EDS pie chart iv). And C, O, N and S are present in deposits shown in e) and f). Scales correspond with TEM images shown in figure 3.

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Introduction

Jet fuel is also used as a coolant in the heat exchanger inside aircraft gas turbine engine and routed through compact sections which increases thermal stress and supports deposition [2]. Soluble macromolecular oxidatively reactive species (SMORS) are deposit precursors and elementary heteroatomic units containing unsaturated and aromatic hydrocarbons. Heteroatomic compounds containing O, N and S are present in trace amounts in jet fuel which as a result of primarily oxidation such as free radical reactions, form nano and micron size solid particles. For example, quinones, pyrroles, indoles, furans and phenols are present in trace levels in the kerosene type fuels. Thermal stressing of jet fuel produces SMORS and deposits. In this work, thermally stressed jet fuel samples are analyzed by spectroscopic and microscopic methods. SMORS and deposit nanostructures and their micron size agglomerates captured by SEM and TEM and spectroscopic analysis revealed higher molecular weight species and heteroatomic deposits.

Methods

Jet A was thermally stressed by flask static tests. Round bottom flask volume was 100 ml and 250 ml with fuel volume 50 ml and 125ml respectively. Temperature was set at 190 ^{0}C and heating time was 6 hours. Oxygen sparge was not provided during experiment. Fuel deposits were separated using hexane because solids are hexane insoluble [1]. Methanol extraction of thermally stressed fuel was conducted prior to mass spectrometric analysis to extract heteroatomic polar components from fuel samples. Spectroscopic methods used to analyze Jet A were high resolution mass spectrometry with electrospray ionization source (ESI-MS), Fourier transform infrared attenuated total reflection (FTIR-ATR) and 13C nuclear magnetic resonance (NMR). Microscopic analysis was conducted with transmission electron microscope (TEM) and scanning electron microscope (SEM) with energy dispersive x-ray spectroscopy (EDS).

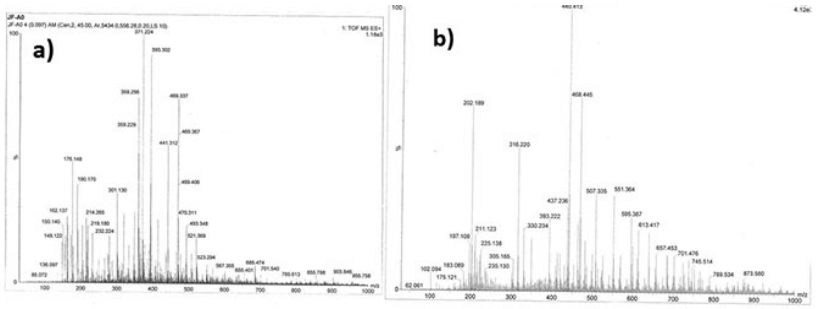

Figure 1: Mass spectra of Jet A thermally stressed samples extracted with methanol showing SMORS in the mass range 300 to 1000 Da.

Results

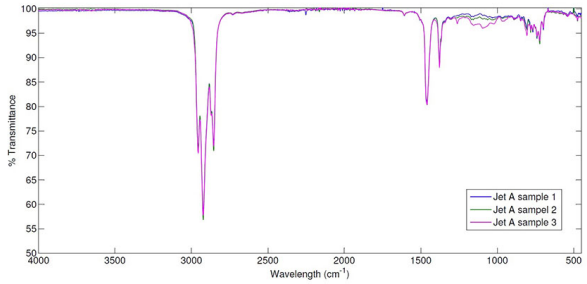

Figure 2: FTIR spectra of Jet A showing additional peaks in the Jet A sample 3 in the 1000 to 1200 cm-1 [3]

Spectroscopic analysis of Jet A SMORS and fuel deposits was conducted by ESI-MS which revealed higher molecular weight species, formed as a result of fuel thermal stressing in the mass range 300 to 1000 Da also known as SMORS. It should be noted that fuel components are also present in the mass range above 300 Da which were originally present in the unstressed fuel and cannot be categorized as SMORS, however such components are relatively much less in concentration. As shown in figure 1a and 1b 1, SMORS are present in thermally stressed fuel (figure 1b) in the mass range above 300 Da with relatively more species compared with unstressed fuel in figure 1a.

FTIR and ^{13}C NMR analysis of Jet A revealed heteroatomic oxygen containing species compared with unstressed fuel samples. Figure 2 shows FTIR spectra with more concentration of alkoxy species in the range 1000 to 1200 cm^{-1} of Jet A sample 3 collected after 6 hours flask test compared with unstressed fuel sample Jet A sample 1, and 2 hours heated fuel sample Jet A sample 2.

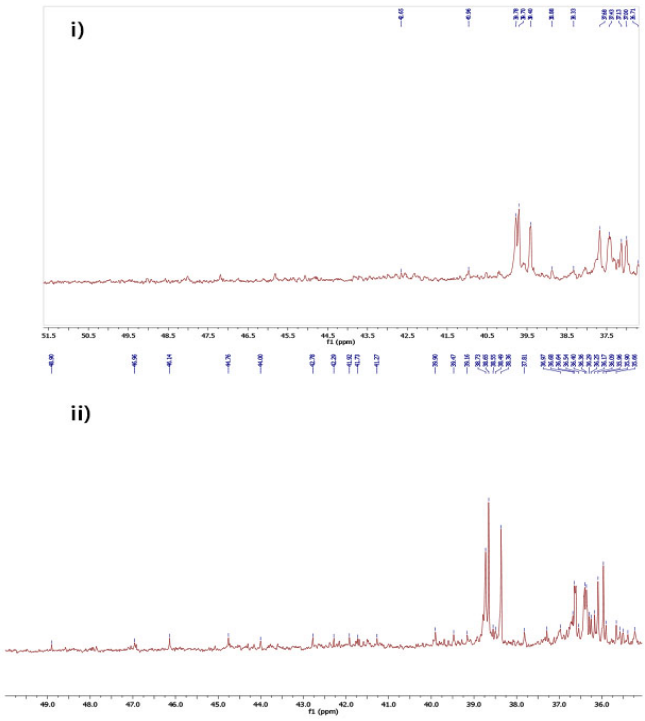

Figure 3: NMR spectrum of thermally stressed Jet A sample with peaks 35- 50 ppm indicating oxygen containing fuel components compared with i) unstressed fuel spectrum [3]

NMR spectra of thermally stressed fuel show heteroatomic peaks with relatively very low intensity as expected because of their low concentration compared with other hydrocarbons in the range 35 - 50 ppm. Figure 3 ii)3 is one dimensional C13 spectra with oxygen containing and heteroatomic peaks in the thermally stressed fuel which are not present in unstressed fuel in the spectrum figure 3 i) 3.

Microscopic analysis of Jet A deposits and their constituent SMORS revealed unit nanoparticles in the range 10 to 30 and 40 to 80 nm. Noticeably, spherical deposits in the 0.5 to 1 micron range are formed as a result of thermal stressing by 6 hours flask tests. Similar results were obtained in four repetitions of experiments. An important observation was the amount of deposition and fuel sample volume. Deposits formed in the flask test by 125 ml volume were less compared with 50 ml fuel tested in the same experimental conditions. Fuel composition contributes in the condensed phase soot formation [4]. Similarly, fuel composition is an important factor in producing SMORS and deposits. Jet fuel thermal stressing was conducted in the autoxidation regime (150 to 300 ^{0}C)

which results in producing fuel free radicals such as $R^{\bullet}$,$H^{\bullet}$, $ROO^{\bullet}$, $OH^{\bullet}$ and supports oxidation reactions. However, longer heating time of static flask tests and fuel containing heteroatomic, aromatics and unsaturated compounds may contribute in supporting condensation reactions. Also, heteroatomic compounds are more reactive than other hydrocarbon species. In summary, qualitative analysis and predicting possible reaction mechanisms is imperative to understand SMORS and deposits formation especially for applications such as hydrocarbon and biomass derived fuel blends with relatively higher heteroatomic content. Exploring alternative reaction mechanism, and varying thermal stressing duration and temperature are in progress and future research goals. NMR analysis of SMORS for structural elucidation is an important next step in this study. Quantitative measurements of deposits along with more microscopic analysis are also in progress.

Conclusions

- Jet fuel samples thermally stressed by flask tests produce heteroatomic deposits with unit nanoparticles. Uniquely, micron size deposits are spherical and made of nanostructures as recorded by SEM and TEM.
- O, N and S are present in relatively less weight % in the deposits compared with C as recorded by EDS.
- Oxygen deprived thermal stressing with longer heating time and morphological similarity of deposit nanostructures with carbonaceous particles suggests investigating similar deposition mechanisms as next steps.

References

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