

Characterization of Deposits Formed on Diesel Injectors in Field Test and from Thermal Oxidative Degradation of n-hexadecane in a Laboratory Reactor

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Abstract

Solid deposits from commercially available high-pressure diesel injectors (hpdi) were analyzed to study the solid deposition from diesel fuel during engine operation. The structural and chemical properties of injector deposits were compared to those formed from the thermal oxidative stressing of a diesel fuel range model compound, n-hexadecane at 160 °C and 450 psi for 2.5 h in a flow reactor. Both deposits consist of polyaromatic compounds (PAH) with oxygen moieties. The similarities in structure and composition of the injector deposits and n-hexadecane deposits suggest that laboratory experiments can simulate thermal oxidative degradation of diesel in commercial injectors. The formation of PAH from n-hexadecane showed that aromatization of straight chain alkanes and polycondensation of aromatic rings was possible at temperatures as low as 160 °C in the presence of oxygen. A mechanism for an oxygen-assisted aromatization of cycloalkanes is proposed.

Introduction

Diesel fuel has a widespread use in engines that vary in size, speed, power output and application. This includes all forms of land, sea and air transportation, power generation units and machinery for industrial use. The thermal stability of diesel is therefore a critical parameter for the smooth operation of these systems. Filter plugging and solid deposit formation on fuel injector tips are the two problems most commonly encountered among diesel engine operators. The formation of deposits has been attributed to diesel instability during storage and engine operation [1]. These deposits can cause serious malfunction or even failure in extreme cases. One of the important features that distinguishes diesel from gasoline and jet fuel is that its chemical composition allows it to be self-igniting. The diesel instability problem is instigated by the presence of highly reactive long-chain paraffins and dissolved oxygen in the fuel.

Studies so far have shown that fuel oxidation products, hydroperoxides and alkylperoxy radicals are primarily responsible for the formation of insoluble deposits from diesel and other middle distillates [1, 2]. This study investigates the nature of hpdi deposits obtained from high-pressure fuel injector. Since information on the hydrocarbon and heteroatom composition of the batch of diesel fuel from which these solids were formed was not available, deposits were characterized and compared in order to learn the

thermal history and formation mechanism of the injector deposits.

Experimental Section

Deposits formed at the tip of commercial high-pressure diesel injectors after at least hundreds of hours of operation were collected and characterized. The surface morphology of the deposits was determined using Field Emission Scanning Electron Microscopy (FESEM). The internal structure of the deposits was determined by polarized-light Microscopy (PLM), Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM). Chemical characterization of the deposits was done using Pyrolysis Gas Chromatography/ Mass Spectrometry (PyGC/MS), Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), X-ray Photoelectron Spectroscopy (XPS) and Thermo-Gravimetric Analyzer- Mass Spectrometer (TGA-MS). A Waters Micromass Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) mass spectrometer was used to determine the molecular weight distribution of the hpdi deposits. A model compound, n-hexadecane was stressed in a flow reactor under thermal oxidative conditions. The reactor used was a ¼ in (OD), 20-cm long, glass-lined, stainless steel tube reactor inserted in a vertical block heater. The temperature and pressure during thermal stressing were set at 160 °C and 450 psi respectively. The start time for the experiment was noted after the fuel bulk temperature reached the wall temperature of 160 °C. The fuel temperature and pressure were kept constant for the duration of the experiment. The thermal stressing was carried out for a period of 2.5 hr in the presence flowing air. The fuel flow rate into the reactor for the thermal stressing experiments was 1.2 mL/min. Based on the fuel flow rate and the reactor dimensions, the total residence time of the fuel in the reactor was calculated to be 77 s. The same experiment was also carried out with 700 ppm of an organic sulfur

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compound, benzyl phenyl sulfide (BPS) added to n-hexadecane to study the effects of sulfur addition, if any, on the formation of thermal oxidative degradation products.

Results and Discussion

The thermal stressing conditions to which the diesel fuel were subjected in the injectors were not known. The results of the chemical and morphological analysis of these deposits are discussed in this section, along with the results obtained from n-hexadecane stressing experiments.

Pyrolysis GC/MS of the deposits helped identify more than 200 compounds. A significant portion of the fragmentation products were benzene and alkylated benzenes. The largest ion seen in a mass spectrum profile of the deposits was coronene – a seven-ring condensed polyaromatic compound. These observations provide further evidence that the deposits consist of relatively large polyaromatic hydrocarbons (with H/C <0.5) and explain why a large fraction of the solid deposits does not dissolve in liquid solvents.

The MALDI analysis was done to obtain the molecular weight distribution of these aromatic solids. The MALDI spectrum of these deposits showed a molecular weight distribution of 82 to 1000 amu indicating that the largest constituents may contain up to fourteen condensed aromatic rings. The compound with a mass of 82 amu is most likely methyl furan. The highest fraction of the deposits seemed to be a homologous series of pyrene starting at a mass of 202 amu. The mass addition of 14 corresponds to the addition of a methyl group to pyrene. Coronene with a molecular weight of 300 amu lies in the middle of the molecular weight range of these deposits.

Examination of Microstructure of Deposits.

In Figure 1, FESEM images show that the hpdi deposits consist of clusters of spherical particles. They form densely packed aggregates and large void volumes between aggregates. Individual spheroids that can be resolved in the clusters appear to have a uniform size distribution.

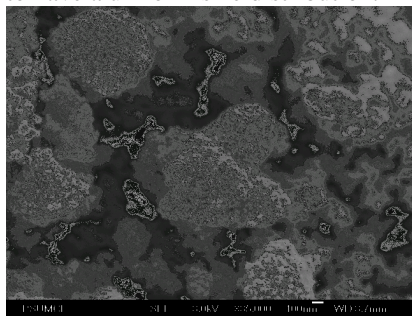


Figure 1. FESEM images of deposits formed at the tip of HP-fuel injector nozzles.

Polished sections of the deposits examined with a polarized-light microscope also show aggregates of densely packed spherical particles (Figure 2a). Different colours observed on the

polarized-light micrographs in Figure 2a result from differences in reflectance of polarized-light depending on the porosity (or bulk density) of the aggregates. All aggregates examined under the polarized-light exhibited an isotropic texture. The flat edges in the particles seen in Figure 2b shows that the deposits were in contact with a substrate- in this case, the fuel injector tip. The spherical morphology of the deposits suggests that they were formed in the liquid phase, deposited on the tip and aggregated into dense clusters. The presence of significant porosity between clusters (or absence of massive solid structures on the substrate) also support the inference that the particles nucleated and grew in the fluid phase and deposited onto the substrates to form the aggregates.

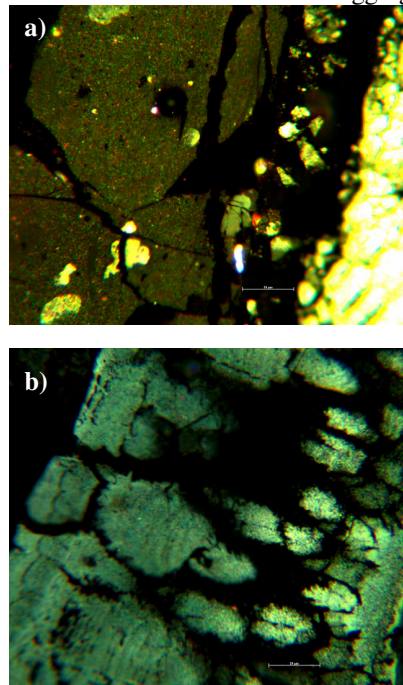


Figure 2. (a) and (b) Polarized-light microscopy images of hpdi deposits

TEM of the hpdi deposits (Figure 3a) also confirm that they consist of aggregated particles that form condensed structures. Figure 3b shows the HRTEM image of a single particle. The individual particles of hpdi deposits show no regions of layer plane alignment in their internal structures.

Spectroscopic Analysis of Deposits. DRIFTS.

The spectrum in Figure 4 shows that the chemical groups present in the commercial hpdi deposits. The bands at 1600 cm^{-1} and 1735 cm^{-1} are assigned to the aromatic carbon-carbon stretch, C=O groups, respectively. The peak $\sim 1200\text{ cm}^{-1}$ corresponds to C-O groups. As discussed in the previous chapter, the presence of C=O and C-O linkages indicate the presence of carboxylic acid, lactone or carboxylic anhydride groups in the deposits [3]. Sauer et al. [4] in their study of sediment formation from the degradation of heating oils, suggested the presence of oxygen functional groups in the form of ester type linkages in the deposits.

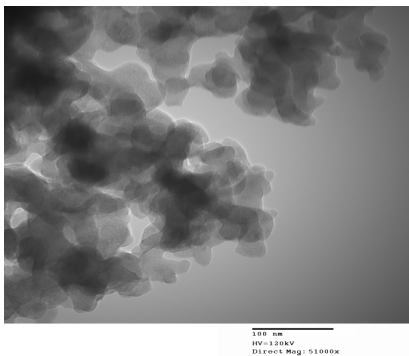


Figure 3a. TEM image of deposits from hpdi at varying magnification.

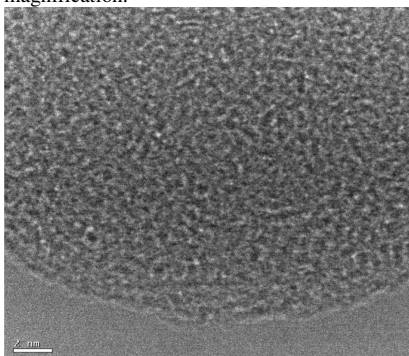


Figure 3b. HRTEM image of deposits from hpdi

The peaks between 700 and 900 cm^{-1} (out of plane bending of aromatic H) indicate the substitution of aromatic-H by other functional groups. The peaks at 893 cm^{-1} , 838 cm^{-1} and 760 cm^{-1} are assigned to isolated aromatic H, two adjacent aromatic H, and 4 adjacent aromatic H respectively. Low intensity of these peaks indicates these deposits are comprised of condensed polyaromatic hydrocarbons. The broad band between 2900 and 3600 cm^{-1} corresponds to -OH stretch. This is a combination of the -OH groups in phenolic compounds as well as water adsorbed on the KBr powder.

The bands at 3050 cm^{-1} , 2970 cm^{-1} and 2850 cm^{-1} which correspond to the aromatic C-H stretch, -CH₃ asymmetric stretch and -CH₂ stretch, respectively, are weak. The low intensity of the aromatic C-H peak at 3050 cm^{-1} is attributed to a relatively high oxygen concentration in the deposits [5]. The weak -CH₂, -CH₃ bands suggest that the aliphatic groups associated with the deposits are negligible. Comparison of the IR spectrum of diesel injector deposits to the IR spectra of the deposits from Jet A thermal oxidative degradation suggests they have a similar chemical composition – condensed polyaromatic structures with single and double bonded oxygen moieties.

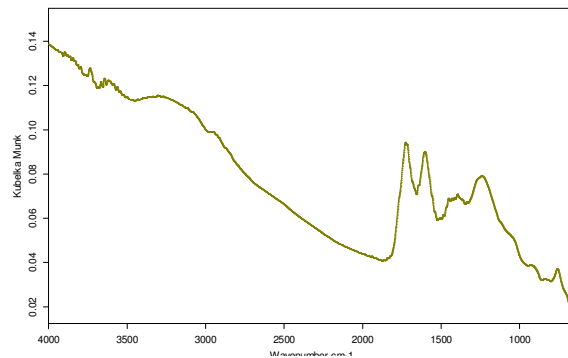


Figure 4. DRIFTS spectrum of hpdi deposits

X-ray photoelectron spectroscopy. The XPS spectrum of the injector deposits is shown in Figure 5a. The binding energy (BE) values of all the peaks in the spectrum were corrected by a charge correction factor corresponding to C 1s peak at 284.7 eV. The XPS spectrum showed only the presence of C and O on the surface of the deposits. The O/C ratio in the deposits was determined to be ~ 0.2. The high resolution C 1s spectrum obtained from these deposits is shown in Figure 5b. This showed three distinguishable components with peaks at 284.7 eV, 286.5 eV and 288.8 eV, respectively. The peak at 284.7 eV corresponds to Ar(C) [6]. This complements the results from DRIFTS analysis of the deposits indicating polyaromatic hydrocarbons. The peak at 286.5 eV is assigned to $\overset{\text{C}}{\text{C}}\text{-O}$. C-O groups indicate the presence of phenolic, furan, alcohol or ether groups. The peak at

288.8 eV is assigned to a $\overset{\text{O}}{\text{C}}\text{-O}$. This peak supports the results obtained from the DRIFTS analysis of the deposits indicating the presence of oxygenated groups such as carboxylic acids, anhydrides or lactones on the deposits. [7, 8, 9]. The TGA-MS analysis of the deposits, discussed in the next section gives information on their chemical reactivity and hydrogen content.

TGA-MS analysis. The CO₂ evolution profile (Figure 6) from the TGA-MS analysis of the hpdi deposits shows that oxidation began around 220 °C and was completed by 750 °C. A shoulder is observed between 400 – 520 °C. The carbon species bonded to the oxygen moieties are expected to be the most reactive components of the deposits, thus being the earliest to oxidize. The CO₂ evolution from disordered and relatively ordered polyaromatic structures occurred around 610 °C and 720 °C respectively. The H₂O evolution profile in Figure 6 shows three peaks, the first one < 200 °C, the second at 450 °C and the third at 600 °C.

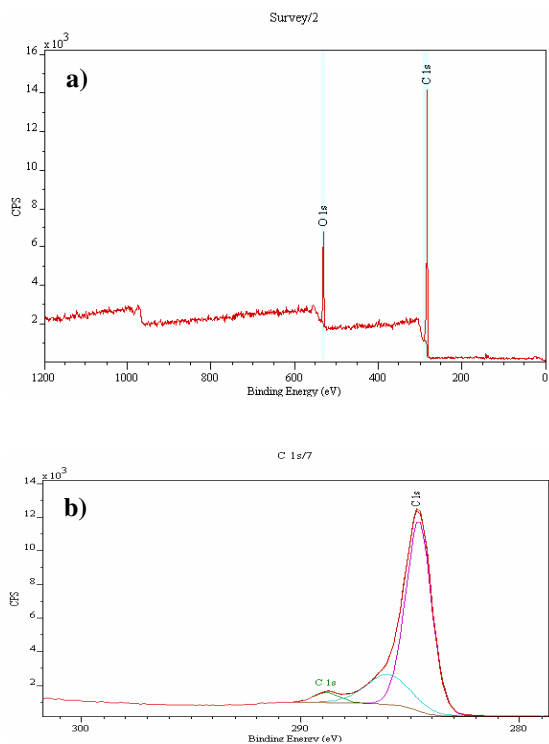


Figure 5. (a) XPS spectrum of hpdi deposits. (b) High Resolution C 1s spectrum of the same.

The peaks at 120 °C can be attributed to the removal of physisorbed water from the deposits. The peaks at 450 °C and 610 °C indicate hydrogen species associated with the oxygenated functional groups and less ordered polyaromatic hydrocarbons respectively [10]. An H/C ratio of ~ 0.4 was obtained from the TGA-MS analysis of these deposits also indicating condensed polyaromatic rings. The high temperature shoulder at 720 °C does not have a corresponding H₂O peak. This indicates that this component of the deposits do not have a significant amount of hydrogen associated with them. This corroborates with the well known fact that structurally ordered solids have very little hydrogen associated with them.

Results from the thermal oxidative stressing of the diesel range model compound n-hexadecane are discussed in the following section.

Characterization of Deposits from the Thermal Oxidative Degradation of n-Hexadecane. Thermal stressing of n-hexadecane at 160 °C and 450 psi in a flow reactor produced a relatively small amount of deposits (0.003 wt% of fuel mass flowed through the reactor in 2.5 h) after 2.5h of thermal stressing.

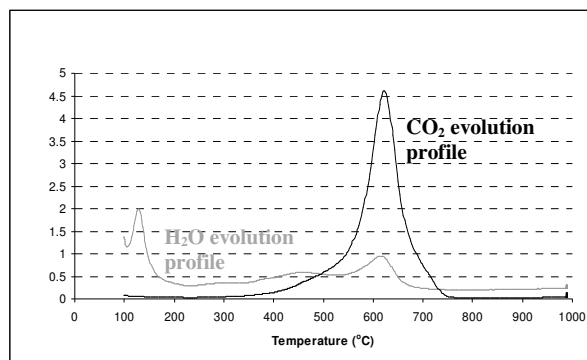
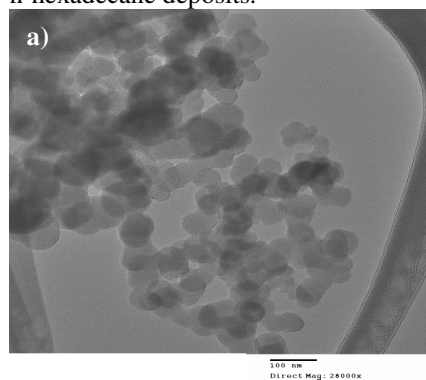


Figure 6. TGA-MS profile of CO₂ and H₂O evolved from the oxidation of carbon and hydrogen species in hpdi deposits from 100-1000 °C

Figure 7 shows the TEM images of deposits formed from the thermal oxidative degradation of n-hexadecane at varying magnifications. The observed spherical morphology once again (Figure 7a), shows deposit nucleation and growth in the fluid phase [11]. The internal structure of the individual spheres was revealed at higher magnifications (Figure 7b). While the interior of the deposit seemed to contain amorphous carbonaceous material, parallel lattice fringes were observed towards the outer portions. These fringes show layers of planar polyaromatic structures. Comparing Figures 7b and 3b one can say that, the structure of the deposits formed from n-hexadecane was similar to those formed from the hpdi with the main difference being a higher fraction of ordered carbonaceous material in the deposits formed from n-hexadecane. The reason for this observation is explained below. This suggests that the hpdi deposits will show a higher oxidation reactivity compared to the n-hexadecane deposits.



During TGA-MS analysis, the peak CO₂ evolution from the hexadecane deposits occurred around 740 °C (Figure 8). This is 20 °C higher than the temperature of CO₂ evolution from the ordered structures in the hpdi deposits.

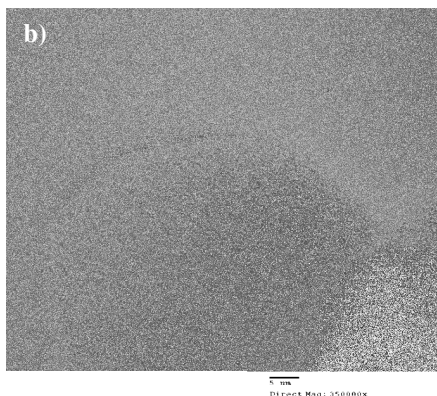


Figure 7. TEM images of deposits formed from the thermal oxidative degradation of n-Hexadecane at 160 °C and 450 psi for 2.5 h at magnifications of (a) 24,000X (b) 350,000X

This result agrees with the observation in the TEM images of the two deposits where a higher degree of structural order was seen in the n-hexadecane deposits compared to the deposits formed from the thermal oxidative degradation of diesel. The higher structural order in the deposits formed from n-hexadecane compared to those from diesel can be attributed to differences in hydrocarbon composition. Carbonaceous solids formed from relatively large aromatic species have an amorphous structure due to growth by the coalescence mechanism [12] while the solids formed from smaller hydrocarbons such as acetylene form more ordered graphitic structures due to controlled hydrogen abstraction-carbon addition (HACA) mechanism [13]. Diesel being a complex blend of aliphatic, cycloalkane and aromatic compounds would tend to form more amorphous structures upon degradation compared to the solid products formed from relatively simple radicals originating from n-hexadecane.

The temperature range for CO₂ evolution from the n-hexadecane deposits was 540 °C to 900 °C. The CO₂ contribution from the most reactive component of the deposits oxidizing around 450 °C in the hpdi is not apparent (Figure 8) in the mass spectrometer profile. In the hpdi deposits, this CO₂ peak was associated with an H₂O peak evolving around the same temperature. The corresponding H₂O evolution peak was however observed in the TGA-MS profile of the n-hexadecane deposits. Hence we can that the CO₂ peak evolving from these deposits between 400 and 500 °C is hidden by the offset in the baseline of the CO₂ evolution profile. The second H₂O peak evolving at 750 °C can be attributed to the hydrogen species associated the polyaromatic hydrocarbons. The spikes in the CO₂ evolution profile at 750 °C and 800 °C can be attributed to the oxidation of capsules of volatiles trapped within the layers of ordered polyaromatic hydrocarbons. We see from Figure 8 that the intensity of the H₂O evolution peak from these volatiles, although visible is significantly low. Such

capsules were also observed in the oxidation profiles of soot formed in diesel engines [14].

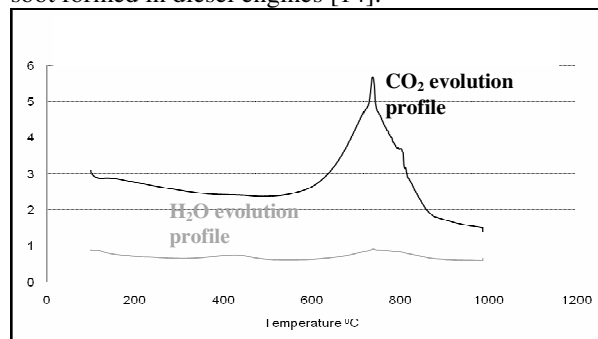
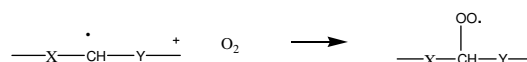


Figure 8. TGA-MS profile of CO₂ and H₂O evolved from the oxidation of solid deposits formed from n-Hexadecane degradation from 100 – 1000 °C in the oxidant stream

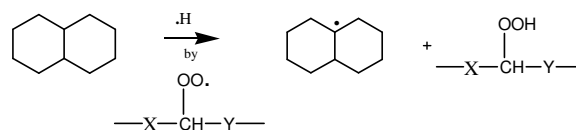
The formation of carbon rich deposits containing ordered polyaromatic structures from the thermal oxidative degradation of n-hexadecane shows clearly that large polycondensed aromatic hydrocarbons can be formed from paraffins at temperatures as low as 160 °C in presence of oxygen.

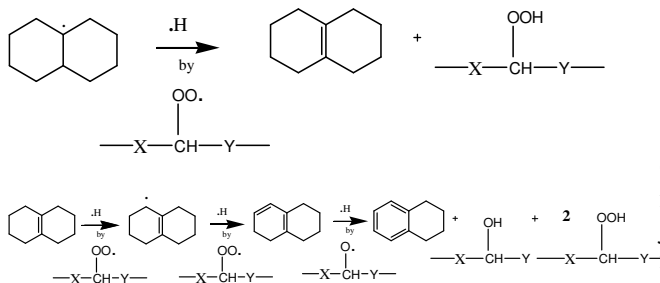
GC/MS analysis of the liquid degradation products details of which can be obtained from the related thesis [15] provides further evidence in this regard. Jensen and co-workers [16, 17] in their study of the liquid-phase oxidation of n-hexadecane proposed that the intermediate hydroxyl and alkylperoxy radicals formed during degradation aid in hydrogen abstraction from the alkane chains. The role of oxygen can thus be compared to that of a catalyst in facilitating low temperature aromatization of aliphatic hydrocarbons.

The literature so far accounts for the presence of cycloalkanes, furans and their derivatives in the degradation products. However, The results presented here show that the solid deposits are primarily aromatic. A mechanism for oxygen assisted aromatization of the cycloalkanes has been proposed. The mechanism of formation of the alkylperoxy and alkoxy radicals which are the proposed hydrogen scavengers has already been described by Jensen and co-workers [18].



Hydrogen abstraction from cycloalkanes is a well known phenomenon [19]. The mechanism for hydrogen abstraction from cycloalkanes by alkylperoxy and alkoxy radicals has been proposed based on the above two steps. The mechanism proposed above shows the conversion of a cycloalkane to a hydroaromatic compound. This can be considered the initial step in the aromatization of cycloalkanes.





As the hydrogen abstraction by alkylperoxy and alkoxy radicals proceeds, the aromatic compounds progressively undergo condensation and polymerization to form large PAHs. The amount of oxygen supplied in these experiments was calculated to be in excess of the amount required to form solids at the reported conversion ratio according to this mechanism. How the oxygenated intermediates participate in the conversion of paraffins to cycloalkanes during the thermal oxidative degradation of the fuel is not clear. Once the cycloalkanes are formed however, PAH formation can increase rapidly due to dehydrogenation by the highly reactive oxygenated intermediates. Dehydrogenation reactions leading to the formation of aromatics from paraffinic compounds so far have been known to occur only at relatively high temperatures (> 400 °C) in the absence of dehydrogenation catalysts [20]. The presence of aromatic solids at temperatures as low as 160 °C suggest that the oxygenated intermediates are responsible for this phenomenon.

Conclusions

The chemical and morphological properties of HPDI deposits showed similarities in structure properties of those formed from the thermal oxidative degradation of a model compound, n-hexadecane in short duration experiments. These results suggest that the deposits formed at the tip of the diesel injector were also formed by oxidative degradation of diesel fuel under similar temperature-pressure conditions. Both kinds of deposits consist of polycondensed aromatic hydrocarbons arranged with varying degrees of structural order in the solid carbons. Both deposits also contained oxygenated functional groups.

Thermal oxidative stressing of n-hexadecane showed that aromatic solids can be produced from n-paraffins at temperatures as low as 160 °C in presence of oxygen. Alkoxy and alkylperoxy intermediates, once formed during the thermal oxidative degradation of hydrocarbons may lead to the formation and aromatization of cycloalkanes by hydrogen abstraction at relatively low temperatures.

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