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Environmental and Biomedical Applications



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CHAPTER 9

Advanced methodologies for remediation of combustion-generated particulate matter (soot) from the environment

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9.1 Introduction

Mortality and morbidity are estimated to be set side by side with air pollution, and these associations are well established between ambient air pollutants and human health. With rapid economic growth worldwide, about one-third of the population has hinged on the burning of biomass and fossil fuels for energy supply. Diesel engines, one of the most economically and commercially viable combustion systems, have been profoundly prominent for their efficiency and unusually popular for the large amounts of malicious pollutants emitted postcombustion. Globally, diesel vehicle emission standards are inclining toward meticulous and stringent policies. These primarily focus on NO_x and soot, being the most malignant, adversely affecting human health, causing acid rain, ground-level ozone, and reducing visibility. Literature suggests a prototypical trade-off relationship between these two, such that the decrease in one consequently provokes a build-up of the other. Although NO_x reduction is being comprehensively addressed and watered-down, mitigation of soot has seen an ineffectual success rate.

Soot is an indispensable component of air pollution, having one of the most extended atmospheric lifetimes and can intensify collectively and spread through air currents over more significant geological regions. It has been held accountable for a considerable measure of environmental damage and has a consequential impact on the healthfulness of living organisms. Diesel exhaust particles constituting their fine and ultrafine nature lead to the inception of oxygen-free radicals (hydroxyl, superoxide, peroxide, etc.) and reactive oxygen species by redox cycles which further undergo a series of mechanisms eventually causing oxidative damage to cellular DNA. Extended exposure to soot is symmetrically related to lung cancer, chronic cardiopulmonary diseases, and furthermore leading to noxious health effects due to modification of cellular components, cellular mutagenicity, etc. [1,2]. Being a heterogeneous system, soot consists not only of organic matter but also inorganic matter such as sulfates, nitrates, etc., along with trace amounts of metals which are picked up by flora and fauna damaging the enzymatic, transport, and binding pathways involved in innumerable life processes [3]. Acute exposure to soot provides a proximal link between soot and coronary artery disease due to changes in coagulation and platelet activation [4]. A toxicological risk assessment was performed by Soriano et al. [5] to classify the genotoxicity and mutagenicity of soot emitted post-combustion of diesel, biodiesels, and a few other fuels. The mutagenicity index was evaluated using the Ames test and genotoxicity activity in human lymphocytes using an alkaline comet assay. The trends obtained after suitably extracting soot organics were similar for genotoxicity and mutagenicity, where biodiesel soot showed comparatively lower toxicity impacts. Although cell damage was observed in both cases, lower DNA migration was observed in the case of biofuel soot, rendering them proportionately less noxious to living organisms.

In order to assimilate the effects of soot on living organisms and the environment, it is fundamental to scrutinize the formation, characteristics, size distribution, and their affiliation with toxicity. This, along with the various characterization techniques involved in the comprehension of soot particles, is meticulously discussed in the following sections. This is followed by research advancements in soot remediation techniques, the challenges faced and proposals to overcome the existing drawbacks.

9.2 Genesis of soot

9.2.1 Physicochemical properties of soot

Soot is a complex carbon compound produced as a result of incomplete combustion, and much effort is put into controlling its generation. These would be incomplete without a thorough comprehension of its nanostructural order and disorder, surface functionalities, elemental and chemical state, and degree of graphitization [6]. Differing engine conditions and fuel compositions impact the nanostructure of soot, which can also possess significant amounts of volatiles and inorganics. Soot constitutes aggregates of pseudo spherical particles with sizes ranging from 10 to 500 nm, where single aggregates comprise of several tens of particles [7]. At a comprehensive viewpoint, soot particles appear as hollow shells enclosed within a graphitized shell. This hollow shell is considerably amorphous, with particles appearing together as aggregates [8]. The particles seem disordered and lack any sort of organization. The graphitized shell is composed of a fine structure of carbonaceous matter with long-range order and perpendicular aromatic polycyclic aromatic hydrocarbon (PAH) layers. It involves a layered stacking of graphene, which is nothing but carbon atoms arranged in a honeycomb structured hexagonal lattice of six-membered rings [9]. The degree of graphitization provides a decisive scaling of soot structural order, analogous with interplanar crystallite sizes, nanocrystallite heights and widths, and fringe length and tortuosity. These soot nanostructures on thermal treatment experience crystallite growth and a higher density with greater stability, leading to decreased reactivity with oxygenated groups to promote soot oxidation. The reactivity is also crucially dependent upon physically or chemically adsorbed functional groups. Thermal treatment of these would result in weakening of these functionalities and a consequent change in the nanostructure, thereby boosting soot reactivity [10].

Researchers Liu and coworkers [10], as a part of their investigation, coupled a thermogravimetric analyzer with a gas chromatograph-mass spectrometer (GC-MS) and post-thermal treatment identified desorption of CO, C₂H₄, C₂H₆, CH₃OH, C₄H₆, C_5H_6 , C_7H_6 , etc., among other species from the discharge gases. These, along with other carboxylic and hydroxyl functional groups, are predominantly present on soot [11,12]. Soot particles are predominantly made up of carbon, and their carbon/hydrogen (C/ H) atomic ratio gives an insight into the material reactivity. At a given fuel concentration, the C/H ratio is proportional to the soot formation temperature and results in greater soot reactivity. However, on fixing the soot formation temperature, no such trend is observed between the fuel concentration and C/H ratios [13]. The fraction of oxygen functional groups in oxygenated additives and biofuels results in a higher concentration of oxygen content in soot samples, resulting in augmented rates of soot oxidation. Therefore, lower C/O ratio is preferential toward enhanced reactivity and higher internal oxidation of soot particles [14,15]. The physicochemical characteristics suggest that they are in a way a direct consequence of the steps involved in the inception, and understanding this is indispensable toward curbing soot production in engine systems.

9.2.2 Models involved in soot formation

With a focus on fundamental soot formation processes during fossil-fuel combustion, it is indispensable to carry out experimental, computational, and numerical studies. Considerable mathematical models are available in the literature for diesel, biodiesels, and other additives being used in diesel engines, the recent ones being proposed by Chen et al. [16], Kashani et al. [17], Li et al. [18], etc. Such soot models have been studied since the 1980s, and on outlining these, it can be contemplated that the experimental conditions involved during the investigation of these models differed in different studies and also differed concerning the fuels and engine systems in use. Most models consider certain assumptions and have a phenomenological basis to complement experimental data. Hence, it is challenging to consider the supremacy of any soot formation model over the other without a universally acceptable data set that can prove the validity of all such existing models. However, the fundamental formation processes of soot after combustion of diesel remains rather consistent, as will be discussed further and has been illustrated in a simplified manner using a schematic in Fig. 9.1 [19].

The formation of soot involves an exceedingly convoluted gaseous—solid phase reaction in which the solid-phase products formed from mostly gaseous phase reactants have no defined physical or chemical structure. The presence of soot in engine exhaust or emission of soot from a flame is a competitive reaction between soot formation and soot oxidation. Fuel is subjected to pyrolysis reactions post-injection into the combustion



Figure 9.1 Schematic illustrating soot formation process.

chamber; however, in fuel-rich regions under sub-stoichiometric oxygen conditions due to incomplete combustion reactions, soot begins to form. Even though crucial details of the formation mechanism are not yet comprehended, the general characteristic steps include (i) Formation of soot precursors, (ii) Nucleation of PAH molecules, (iii) Gaseous reaction induced mass growth, (iv) Coagulation of solid-phase species, (v) Graphitization of particles, (vi) Oxidation of soot particles to form gaseous products [19].

A precursor is essentially a substance from which another is formed. Principal soot precursors include poly-acetylenes, ionic species, or PAH, and these include aromatic molecules which are themselves toxic and do not comply with environmental regulations. Following pyrolysis, higher hydrocarbons from fuels get hydrogenated into lower hydrocarbons, and their radicals which consequently dehydrogenate to result in formation of acetylene (C_2H_2) and other unsaturated compounds. These molecules further polymerize to form poly-acetylenes and are subjected to cyclization under the exhaust temperature and pressure conditions. The abundance of C_3H_3 and $n-C_4H_3$ radicals serve as excellent precursors for phenyl ring formations which follow reversible H-abstraction reactions to form benzene rings [20]. In-depth chemical particulars of these nascent soot nucleation processes are not yet comprehended thoroughly due to experimental limitations. Depending on the precursors formed [21,22], the growth process proceeds to the formation of PAH molecules, wherein molecules convert into larger particulates having diameters smaller than ~ 10 nm. These particles further undergo gas-phase radical

reactions, and surface growth proceeds gradually. This surface growth process is directly dependent upon the composition of the fuel, i.e., the amount of saturation in carbon bonds, the carbon chain lengths, and the elemental compositions, and in particular on the inherent oxygenated radicals formed in the mixture post-combustion. This, however, won't have a major effect on the number of particles, and the particles formed constantly collide, causing a substantial increase in particle diameter and the consequent outcome being a reduction in the number of particles. The process occurs in the premature particle stage as once the particles begin to mature, the particles merely stick to each other, and it proceeds with carbonization reactions involving ring fusions and condensations, cyclization, elimination of functional groups, and dehydrogenation, along with growth and alignment of PAH stacked layers [9,19,23].

Now, at this stage, gradually, graphitization comes into play, and the amorphous soot material progresses toward a higher orderly arrangement, and eventually, the number of active sites reduces, thus, decreasing surface reactions. The final step in the soot production cycle ironically isn't a growth process but an elimination one in which soot oxidation reactions occur on the particle surfaces via heterogeneous reactions causing mass loss and forming CO_2 , CO_3 , and H_2O_3 . Depending on the flame or combustion system, oxidation may occur throughout simultaneously along with formation. It could be assumed to be a competitive reaction between soot particle growth with concurrent oxidation of these same particles. Fuel bound oxygenates such as CO₂, H₂O, NO, N₂O, NO₂, etc., transfer O atoms from gas to solid phase forming complexes which decompose, losing a C atom from the surface, given out in the form of CO or CO_2 . Maintaining fuel/oxidant ratio enhances internal oxidation of fuels leading to faster fuel oxidation rates, greater disordered soot with reduced particle size, and also enhancing fuel economy. A trade-off relationship between soot formation and oxidation leads to a wider range of size distribution in soot particles, and different size leads to different outcomes, which will be highlighted in the following section [24,25].

9.2.3 Size distribution of particulate matter and their biochemical toxicology

The great smog of 1952 killed a myriad of citizens in London, while a similar fate was that of the Donora smog. Among the fundamental components of smog, soot is one of them. It is not only detrimental to human life but also to plants and crops, also contributing toward global warming. Soot, although invisible to the naked eye, interacts with light and reduces visibility during smog events, also with its regional cooling effect which is particle size and composition dependent, it contributes to climate change [26]. The size of these particles thus plays a vital role in environmental and biological effects involving PM. Living organisms get exposed to PM primarily via dermal contact, ingestion, or respiration, in which PM causes chronic ailments, and the condition further worsens as a result of deposition and bioaccumulation. The size of the particles predestines the distribution and rate of deposition once the particles are in the system. Larger particles typically settle

Size	Biological toxicity	
Coarse particles (PM ₁₀), $\leq 10 \ \mu m$	Epithelial dysfunction and exacerbation, asthma, chronic obstructive pulmonary disease (COPD) [27], cell viability, necrosis, apoptosis, DNA lesions and cell cycle arrest, severe genotoxic and prenecrotic effects [28], increase in pericardial sac area and bulbus arteriosus distance in zebrafish [29].	
Fine particles (PM _{2.5}), $\leq 2.5 \ \mu m$	Cell membrane lysis, mitochondrial ultra-structural disruptions, cell mortality and ultra-structural lesions [30], water-soluble fractions increase reactive oxygen species, mitochondrial transmembrane potential disruption [31], cytotoxicities in human hepatoma cells, human fibroblasts, embryonic lung fibroblasts [32].	
Ultrafine particles (>0.1 µm or 100 nm	Post lung deposition in rodents, ultrafine particles escape alveolar macrophage surveillance gaining access to the pulmonary interstitium [33], inflammatory response and systematic distribution to extra-pulmonary tissues in rats [34], development and exacerbation of diseases such as bronchial asthma, lung fibrosis and depletion of glutathione and protein-bound sulfbydryl groups producing reactive oxygen species [35]	
Nanoparticles, <50 nm	Proinflammatory effect in lungs by increased cytokine/chemokine production and adhesion molecule expression acts as an adjuvant for allergic sensitization [36], depressive behaviors, systemic fat gain, insulin resistance, metabolic dysfunction, glutamatergic deficits in mice [37].	

 Table 9.1 Correlation of the size of particulate matter with biological toxicity.

in the pharyngeal airway, while finer ones tend to concentrate in the bronchioles and alveoli; finally, the ultrafine particles having longer retention time in the lungs enter the bloodstream affecting mental and physiological wellbeing. The correlation of the size of PM with some of the serious toxicological effects have been illustrated in Table 9.1; however, discussing the toxicity of soot in detail is beyond the scope of this chapter. Nonetheless, readers are directed to Refs. [5,38] for further reading.

9.2.4 Soot particle analysis techniques

Carbonaceous particles formed during combustion scenarios have been meticulously examined during the past centuries. In order to approach an abridged representation, it is thus obligatory to consider the bizarre interaction of soot particles with electromagnetic radiation as well as morphological visual inspection techniques. This endorses the comprehension of the physicochemical characteristics of soot along with understanding its oxidative reactivity, nanostructural characteristics and chemical organization. The morphological characterization of soot particles is primarily achieved using highresolution transmission electron microscopy (HRTEM) analysis, in which the electrons transmitted from a sample are detected to form an image. The morphology, inner structural characteristics, and particle size can be recorded and it is well known these particle characteristics change depending upon the engine operation, flame temperature and combustion system, fuel and lubricant composition, and on the atmosphere in which the soot particles are formed [39]. HRTEM also gives an insight into the nanostructure of soot where the core—shell structure of each primary particle can be observed with its composition of curved fringes of shorter length in the core representing a higher degree of disorder as compared to the shell with long-range fringes concentrically arranged along the perimeter. Besides, the mean diameter of these primary particles can be found at ~ 100 nm magnification using softwares such as imageJ. Additionally, quantitative analysis of fringe lengths and fringe curvature (tortuosity) at high magnification can be carried out using a set of equations in a MATLAB algorithm put together in a code as given by Yehliu et al. [40,41]. Shorter fringe length and largely curved fringes indicate higher disorder and amorphous structure and therefore are desirable for fast Diesel Particulate Filter (DPF) regeneration, as they have a higher affinity toward oxidative behavior. HRTEM images at different magnifications along with processed data can be found in Fig. 9.2



Figure 9.2 HRTEM images developed at (A) 100 nm, (B) 50 nm, and (C) 5 nm along with the primary soot particle size distribution and MATLAB fringe analysis data for soot of fuel-methyl butyrate blended with diesel and (D–F) for pure diesel soot, respectively. (*Reproduced with permission from S. Da Costa, A. Salkar, A. Krishnasamy, R. Fernandes, P. Morajkar, Investigating the oxidative reactivity and nanostructural characteristics of diffusion flame generated soot using methyl crotonate and methyl butyrate blended diesel fuels, Fuel 309 (2022) 122141. https://doi.org/10.1016/J.FUEL.2021.122141, Copyright 2022 with permission from Elsevier.)*

wherein the images depicting diesel soot have greater mean particle diameter in comparison to soot collected from diesel blended with a saturated oxygenated surrogate.

X-ray diffraction (XRD) analysis, which is dependent upon the constructive and destructive interference of monochromatic X-rays, illustrates details regarding the crystalline structure of the soot samples with two peaks appearing at the 2θ values of ca. 24.5 degrees and ca. 44 degrees assigned to the 002 plane and 100 planes, respectively. Interaction between the sample and incident rays lead to diffraction of these rays and effects the intensity and broadening of the (002) and (100) peaks. The 2θ values shift toward lower values in comparison to the XRD plot of a pure graphite sample indicating greater crystallite disorder due to randomized orientation of the PAH nanocrystallites. Additionally, soot samples show broader peaks due to particle size reduction. If the soot sample is subjected to XRD analysis without appropriate heat treatment, an additional high-intensity peak called γ -band is observed at ca. 19 degrees, which could be attributed toward aliphatic structures which are loosely attached to the soot structural surface as illustrated in Fig. 9.3A [42]. Appertaining to soot studies, analysis of the peaks reveal structural information analogous to the nanocrystallites present in soot samples such as PAH interlayer spacing (d_{002}) , the nanocrystallite height (L_c) , which gives the thickness of the PAH stack and the nanocrystallite width (L_a) , providing the mean PAH stack size as illustrated in Fig. 9.3B. These equations are illustrated as E1, E2, and E3, respectively. While the PAH interlayer spacing can be obtained from Bragg's law, the other two parameters, L_{c} and L_{a} , can be evaluated as per the Scherrer formula as given below,

$$d_{002} = \frac{\lambda}{2\sin\theta_{002}} \tag{E.1}$$

$$L_a = \frac{0.9\lambda}{\beta_{002}\cos\theta_{002}} \tag{E.2}$$

$$L_c = \frac{1.84\lambda}{\beta_{100}\,\cos\,\theta_{100}}\tag{E.3}$$

In accordance with the above equation, λ is the wavelength of X-ray, θ_{002} and θ_{100} are the Braggs angles, and β_{002} and β_{100} are the full width at half maximum (FWHM) for both peaks observed [43]. While XRD analysis is restricted toward evidencing only the crystalline phases, Raman spectrometry presents an advantage by analyzing all kinds of carbon structures in the samples, i.e., crystalline and amorphous phases.

In Raman spectroscopy, light interacts with molecules and the energy of the dispersed photons are used to detect vibrational, rotational, and other states of a system enabling one to interpret the chemical state of the system. For carbon-based soot, the most bene-ficial region of observation is from 800 to 1800 cm^{-1} of the Raman spectrum as depicted in Fig. 9.3C. The spectrum depicts two characteristic peaks, one at ca. 1350 and another



Figure 9.3 (A) XRD pattern of biodiesel blended with diesel before and after heat treatment. (B) PAH interlayer spacing (d_{002}) , the nanocrystallite height (L_c) , and the nanocrystallite width (L_a) . (C) Raman spectra of diesel soot. (D) Electron energy loss spectra of diesel soot. (E) Typical FTIR spectrum of diesel soot. ((A) Reproduced with permission from P.P. Morajkar, M.K. Abdrabou, A.V. Salkar, A. Raj, M. Elkadi, D.H. Anjum, Nanostructural disorder and reactivity comparison of flame soot and engine soot using diesel and jatropha biodiesel/diesel blend as fuels, Energy Fuels 34 (10) (2020) 12960-12971. https://doi.org/10. 1021/acs.energyfuels.0c02063, Copyright 2020 with permission from American chemical Society. (B) Reproduced with permission from M. Lapuerta, J. Rodríguez-Fernández, J. Sánchez-Valdepeñas, Soot reactivity analysis and implications on diesel filter regeneration, Prog. Energy Combust. Sci. (May 1, 2020) 100833. https://doi.org/10.1016/j.pecs.2020.100833, Copyright 2020 with permission from Elsevier. (C) Reproduced with permission from S. Da Costa, A. Salkar, A. Krishnasamy, R. Fernandes, P. Morajkar, Investigating the oxidative reactivity and nanostructural characteristics of diffusion flame generated soot using methyl crotonate and methyl butyrate blended diesel fuels, Fuel 309 (2022) 122141. https://doi.org/ 10.1016/J.FUEL.2021.122141, Copyright 2022 with permission from Elsevier. (D) Reproduced with permission from P.P. Morajkar, G.D.J. Guerrero Peña, A. Raj, M. Elkadi, R.K. Rahman, A.V. Salkar, et al., Effects of camphor oil addition to diesel on the nanostructures and oxidative reactivity of combustiongenerated soot, Energy Fuels 33 (12) (2019) 12852–12864. https://doi.org/10.1021/acs.energyfuels. 9b03390, Copyright 2019 with permission from American Chemical Society. (E) Reproduced with permission from M. Salamanca, F. Mondragón, J.R. Agudelo, P. Benjumea, A. Santamaría, Variations in the chemical composition and morphology of soot induced by the unsaturation degree of biodiesel and a biodiesel blend, Combust. Flame 159 (3) (2012) 1100-1108. https://doi.org/10.1016/J.COMBUSTFLAME. 2011.10.011, Copyright 2022 with permission from Elsevier.)

at ca. 1590 cm^{-1} parallel to the *D* and *G* band, where the *D* band is synonymous to a disordered structure and is associated with the aliphatic content found primarily in the core of the soot structure, while the *G* band corresponds to a rather graphitic structure along the peripheral outer shell of the particles. The two peaks are subjected to

deconvolution, in order to enhance accuracy in calculations using Voight peak fitting as proposed by Catelani et al. [44] Among the resultant five fitted peaks, D1, corresponds to lattice disorder and has the highest intensity, D2 and D3 correspondingly indicate lattice vibrations and amorphous carbon linked to organic molecules and D4 is related to the carbon—carbon stretching frequencies. The proportional value of the D1 and G band are akin with defects in carbon structure and indicate degree of disorientation in the basal planes of the graphitic layers [45]. The ratio of D1 and G can be co-related to the lattice width (L_a) obtained in XRD analysis, as suggested by Escribano et al. [46] using the Knight and White equation as given below in (E.4), a proportionality constant of 4.4 is accepted for an excitation wavelength of 514 nm as given in Ref. [47].

$$L_a = 4.4 \left(\frac{I_{D1}}{I_G}\right)^{-1}$$
(E.4)

Electron energy loss spectroscopy (EELS) technique is also an efficient means to examine disorderliness and graphitic characteristics along with aliphatic/aromatic structural composition of the particles. Statistically, these can be estimated based on quantitation of the peak structures and the relative intensity ratios of the 1s to π^* and 1s to σ^* K edge transitions on soot particle surfaces. This spectroscopic technique basically targets inelastic interactions of electrons from the sample with primary beam electrons. The π^* peak at ca. 285 eV is indicative of C=C bond from aromatic ring structures and is known as the graphitic peak, whereas the σ^* peak at ca. 290–305 eV is indicative of graphitic layer ordering as illustrated in Fig. 9.3D. The peaks appear sharp for lower oxygenated fuels and less developed with broader humps for higher oxygenated fuels which is affirmative of higher disorder in graphene layers, which is well presented in Ref. [15]. Additionally, the ratio of π^*/σ^* allows a comparative classification of aromatics and aliphatics in soot, where a higher ratio suggests lower aliphatic content with higher aromatic content (π bonding) and vice-versa [48,49]. In consideration, since aliphatics oxidize rapidly in comparison to aromatics, greater aliphatic content is highly convenient to facilitate lower temperature oxidation. This will further result in lower activation energy for oxidation of soot into gaseous products. Thermal gravimetric analysis (TGA) in oxidative environment is used to comprehensively examine the oxidation characteristics of soot and to determine its kinetic parameters. It does so by analysis of changes in the sample weight which is directly related to its decomposition and other physicochemical changes under controlled temperature and atmospheric conditions. The oxidative reactivity in oxygen atmosphere is dependent upon the receptivity of edge carbons which have greater reactivity in comparison to basal plane carbon atoms. Presence of five-membered rings results in increased strain therefore greater curvature of bonds resulting in faster oxidative reactivity. Soot oxidation in ambient air is critical toward DPF regeneration as lesser the activation energy, greater will be the DPF regeneration efficiency. Soot oxidation kinetic parameters by TGA will be discussed in the subsequent sections [48,50].

Elemental analysis, based on complete combustion of sample by flash combustion based on the Duman method [52] for determination of carbon, hydrogen, nitrogen, and sulfur can be carried out independently using a CHNS analyser. Post-combustion, the gases are chromatographically separated and detected by thermal conductivity. The H/C ratio can be calculated to define the C–H active sites for oxidative attack, similarly, the C/O ratio is essential as the percentage of oxygen functional group has a direct influence on the soot oxidation kinetics. Another spectroscopic technique to evaluate the C/O ratio involves coating the samples with Au/Pd by sputtering and subjecting it to Energy Dispersive X-ray Spectroscopy (EDS) in which the atomic and weight percentages of carbon and oxygen in various regions of soot can be quantified. Here the target electrons are knocked off using X-rays resulting in positively charged holes which attract other electrons to fill up the vacancy. The energy released in the form of X-rays gives specific information with respect to the elements under study. The physical adsorption and specific surface area can be estimated using the Brunauer-Emmett-Teller (BET) gas adsorption-desorption isotherm studies. This method approximates the degree of adsorption on a given particle by measuring the amount of a gas, usually N₂, at a fixed temperature. The isotherm is thus obtained and its nature reveals details regarding the adsorption process and is related to the pore sizes. Higher surface area indicates greater possibility for O_2 adsorption and diffusion throughout the internal surface structure of the particles [48,53]. In order to identify the surface compounds on soot particles infrared technique (with Fourier transformation) is used to monitor the interaction of their radiation with soot. Post absorption of radiation in the range of $4000-400 \text{ cm}^{-1}$, which produces a molecular vibration due to changes in the dipole moment corresponding to the stretching or bending modes of the bonds present in the surface functionalities. However, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is more fitting for soot as the diffuse reflectance produced is collected with minimum reflection losses especially in case of pulverized samples such as that of soot [53]. A quintessential FTIR spectrum of diesel soot is exemplified in Fig. 9.3E.

In order to analyze the metal content distribution in soot, the samples can be subjected to ICP-MS analysis in order to comprehensively systematize the transferral of metals from fuel or additives to soot which could be in the form of elemental metals, organometallic complexes, metal sulfates, or crystalline metal oxides. When these enter biological systems they further increase toxicity levels beyond normal PM toxicity as discussed previously [12]. Small Angle X-ray Scattering (SAXS) can be utilized to classify the shape, size, and fractal dimensions of the particles, whereas particle sizers such as electrical low-pressure impactors (ELPI), exhaust particle size spectrometers (EEPS), etc., have been used for measuring particle size based on aerodynamic nature. Similarly, NMR techniques such as ¹H-NMR and ¹³C-NMR could be used to perceive the functionalities present on the soot surface. Although all these ex situ techniques are thoroughly utilized, there is a need to minimize the perturbations relating to the combustion environment along with allowing higher resolution for monitoring of molecular species and particles. Therefore, numerous in situ diagnostic methods are being used for accurate analysis of soot. These have been comprehensively summarized in a review by Michelsen et al. [54]. All these techniques display results which help in enhancing the understanding toward a complete overview of soot formation and reactivity. However, a few ambiguities and contradictions still exist and hence other analysis techniques have to be employed to collect less obscure and more reliable data [48,55].

9.2.5 Kinetic rate studies of soot surface growth and oxidation

As discussed earlier, soot is a carbonaceous material formed from the gas-phase nano-sized organic carbon during gas to solid particle transformations resulting in construction of larger-sized elemental carbon particle aggregates. In addition to consistent descriptions of gas-phase chemistry, most advanced kinetic models describe a coupling relation between gas-phase chemistry and aerosol dynamics which comprise of benzene and PAH formation. Once fuel is pyrolyzed, aromatic rings such as benzene and phenyl are formed from acetylene, propargyl, cyclopentadienyl, and other such olefinic groups along with a fundamental role played by Resonance-Stabilised Free Radicals (RSFRs). These have comparatively higher stability in comparison to ordinary free radicals due to the delocalization of unpaired electrons along the conjugated system. However, the addition of these to other radicals result in relatively larger rates with minimal difference in the energetic barrier. These bonds formed are usually weaker but undergo rapid cyclization at elevated combustion temperatures to form benzene/phenyl systems. This is followed by progressive molecular growth and sequential addition of olefins predominantly through the hydrogen-abstraction-carbon addition (HACA) mechanism. Larger PAHs formed here go on to further form the initial soot nuclei and this is the most probable explanation for this gaseous to solid particle growth conversion as this growth can hardly be observed experimentally and thus is profoundly dependent upon phenomenological explanations [56,57].

In accordance with the HACA mechanism, post-abstraction of a hydrogen atom from benzene forming a phenyl radical, a two-step process involving acetylene addition occurs leading to naphthalene formation and further this reaction proceeds via abstractions and addition reactions forming fused polycyclic aromatic rings. These rings further condense to form peri-condensed aromatic compounds (PCAHs), with π -bonds among carbons and reasonable extents of conjugations. Lower hydrogen content in these systems leads to greater condensation and the H/C ratio in these plummet to very low values as the growth progresses. If this growth advances indefinitely, a perfect graphite structure is formed. However, the PAHs not only constitute six-membered rings to form planar structures but also contains five-membered rings. These five-membered rings lead to molecular distortion and consequently result in a reasonable curvature (also called tortuosity) in the soot particle fringe structure. These curved structures are beneficial for faster soot oxidation as they allow rapid oxidative breakdown of the soot structure [57].

As the PAHs continue to grow at a given point they can no longer be considered as gas phase compounds and are categorized as soot nuclei. The gas phase PAHs are usually pyrene like structures subjected to stacking processes where the aromatics stick together and the sticking efficiency is of a magnitude 3-4 times less than unitary value. Despite this low probability among millions of nuclei formed at higher temperatures, nuclei are bound to grow by this clustering of aromatic compounds. This coagulation is considered to be an irreversible reaction and is expected to follow the kinetic collision theory. The particles further interact with the encircling environment and undergo dehydrogenation and addition reactions and further coagulate with other particles thus reducing free surface area and minimizing free energy. As this development progresses, the agglomeration steps advance and the competition between agglomeration and coalescence is dependent upon temperature and chemical characteristics of the molecules. The final stage involves removal of mass from the particle by chemical reactions involving hydroxyl radicals and oxygen, i.e., simply known as oxidation. At this point, carbon atoms are ejected out from agglomerates and oxidizing species sometimes even penetrate into particles internally oxidizing them consequently resulting in breaking up or fragmentation of larger agglomerates into smaller aggregates. Based on the TGA analysis carried-out in zero air a thorough understanding on soot oxidation kinetics has been constructed to investigate oxygen-stimulated soot oxidation. The soot conversion (α), computed as a function of temperature at varied heating rates of $1,3,5,7^{\circ}$ C/min, is given as (E.5)

$$\alpha = \frac{(M_{\rm O} - M_T)}{(M_{\rm O} - M_L)} \tag{E.5}$$

where $M_{\rm O}$, M_T , and M_L correspond to initial soot mass, partially oxidized soot mass, and leftover soot mass and the activation energy, E_a , of this oxidation process can be estimated by the Friedman method [58,59]. The rate of soot conversion $\left(\frac{d\alpha}{dt}\right)$ and soot conversion (α) can be associated using Eq. (E.6),

$$\left(\frac{d\alpha}{dt}\right) = k\left(T\right)f(\alpha) \tag{E.6}$$

where in accordance with the Arrhenius equation, k(T) is the rate constant given by, $k = Ae - (\frac{Ea}{RT})$, while E_a is the activation energy, A and T, the preexponential factor and temperature for soot oxidation, correspondingly. The conversion function is given by $f(\alpha)$, this term rules out the need for individual oxidation reactions as the concentration of O₂ is kept steady through the TGA experiments. The plots obtained from these calculations have been represented in Fig. 9.4. Man et al. [60] concluded that higher the oxygen content in soot results in increased evaporation rate of loosely bound volatile



Figure 9.4 (A) Soot conversion, α , for diesel soot, (B) soot conversion rate ($d\alpha/dt$) at different heating rates, and (C) activation energy at different soot conversion levels for diesel soot represented as D, and unsaturated and saturated surrogate blended diesel fuels represented as MC and MB, respectively. (*Reproduced with permission from S. Da Costa, A. Salkar, A. Krishnasamy, R. Fernandes, P. Morajkar, Investigating the oxidative reactivity and nanostructural characteristics of diffusion flame generated soot using methyl crotonate and methyl butyrate blended diesel fuels, Fuel 309 (2022) 122141. https://doi.org/10.1016/J.FUEL.2021.122141, Copyright 2022 with permission from Elsevier.)*

materials and induces internal oxidation in the soot structure. This can be graphically observed in Fig. 9.4C, wherein the activation energy of oxygenated biodiesel surrogate fuels is lower than that of neat diesel. Additionally, higher activation energies along with higher temperatures are required for oxidation of graphitized peripheral regions of the soot. Greater surface and internal oxidation rate facilitate smoother soot mitigation in DPF filters. In the following sections the different remediation methods and protocols for soot mitigation will be thoroughly discussed.

9.3 Latest research and development in the remediation of combustion generated soot

9.3.1 Catalytic convertors and diesel oxidation catalysts

Catalytic convertors are pollution control devices placed inside the tailpipe of a vehicle through which noxious exhaust gases containing hydrocarbons (HC), CO, NO_x, etc., are emitted. Its fundamental function is to convert these gases into H₂O, CO₂, N₂, and O₂ and currently it is a mandate for all automobiles pursuing on roads. It is a vehicle controlled device and its performance is dependent upon the type of catalyst used in the assembly and the consequential effect of these on the rate of the chemical reactions. The catalyst being a mere mediator reducing the activation energy of the reaction and not being transformed so it can be regenerated and reused during consequent cycles. A catalytic convertor is either a two-way or a three-way device, wherein a two-way convertor has two simultaneous functions, i.e., oxidation of CO to CO₂ in presence of O₂ and oxidation of HCs formed from unburnt and partially burnt fuel into CO₂ and H₂O. However, due to their ineffectuality in NO_x control and the NO_x emission control requirements imposed in the late 1970s they were outmoded by three-way catalytic (TWC) convertors, which simultaneously reduce NO_x to N₂ and O₂, oxidize CO to CO₂, and oxidize unburnt HC to CO₂ and H₂O. These were first introduced in the early 1980 model year vehicles and the catalytic reactions mostly involved noble metals due to their exceptional thermal stability, depreciated ability to react with support materials or base device metals and their sintering resistance capacity [61-63]. These TWC have been used in spark-ignition engines during the past decades, while Diesel Oxidation Catalysts (DOCs) have been used in combustion-ignition engines since the 1990s. The DOC is akin to TWC and both have similar shape, function, and contents. Due to engine compression ratios, ambient temperatures and pressures and inadequacy to maintain high efficiencies in fuel combustion, hydrocarbons escape into the atmosphere as soot and DOCs are essential to curb these HC liberations. Diesel combustion systems possess a selective catalytic reduction (SCR) system, or Lean NO_x traps for NO_x reduction with active metal-based catalysts dispersed on ceramics possessing highly porous structures, within which acidic sites lie on which reductions occur [64].

The preeminent function of DOCs is to oxidize HC and CO as seen in the form of a schematic in Fig. 9.5A, apart from this it is also fundamental in lowering the mass % of diesel particulate emissions by oxidation of HCs adsorbed on the surfaces of soot. DOCs are also influential in facilitating the oxidation of NO to NO₂, thereby increasing the NO₂/NO_x ratio, which is integral for developing the performance of downstream components such as DPF and SCR, along with oxidation of unchecked species such as



Figure 9.5 Schematic of (A) diesel oxidation catalyst (DOC) and (B) diesel particulate filter (DPF). (C) General scheme of PAH oxidation on active sites of support catalyst.

aldehydes and also reducing the odor of diesel exhaust. The oxidation of CO and HC being highly exothermic raises the temperature of the exhaust gas downstream to the DOC, and this further assists in DPF regeneration [65,66]. The DOC is typically the first exhaust component after the engine and their structure is based on cordierite (ceramic) honeycomb-like monoliths. The metal catalyst is dispersed on a high surface area material, known as a wash-coat, which is adhered to the surface of the monolith. The ceramic monoliths however show low porosity despite their remarkable strength, thus nowadays replacing them with metal monoliths [67]. Most commercially available DOCs employ Pt—Pd catalysts where Pd is alloyed with Pt to reduce sintering and improve performance by formation of amalgamate [68]. The accepted mechanism for HC oxidation on this catalyst is the Langmuir—Hinshelwood dual-site mechanism, where physical trapping and oxidizing of volatile components of soot is possible during surface reactions between adsorbed HC and adsorbed O_2 [69]. Current research focuses on improving these catalysts to achieve higher efficiency and durability.

Ho and coworkers [70] examined the role of Pd-Pt interactions in bimetallic Pd-Pt/ γ -Al₂O₃ DOCs. The Pd/Al₂O₃ catalyst exhibited high activity for HC oxidation, while Pt/Al₂O₃ by itself efficiently oxidized NO. The catalyst retained stability and also favored spill over of SO_2 to the alumina support, enhancing the endurance of the catalyst. In another investigation, Ho et al. [71] focused on using zeolites instead of Al₂O₃ as supports for DOCs and investigated the outcome of silica-alumina ratio (SAR) of beta zeolites on the physical, chemical, and oxidative characteristics of Pt–Pd supported catalysts. It was noted that lowering of aluminum content of the support resulted in lower acidity and subsequent reduction in the dispersion of both metals. An increase in SAR increased the Pt fraction in the Pt-zeolite catalyst and emerged with better oxidation of C_3H_8 and C_3H_6 . Extraordinarily, the zeolite-supported Pt and Pd catalyst showed higher oxidative stability in comparison to Pt/Al₂O₃ and Pd/Al₂O₃. Although the former did not show as good sulfur resistance as the latter. Tang et al. [72] employed a surfactantfree hydrothermal method to grow ceria arrays onto a 3D cordierite honeycomb monolith. Furthermore, they reincorporated Al and Si atoms leached from cordierite into the CeO₂, eventually recrystallizing Ce-Al-Si composite nanoflake structures. Lastly, sizecontrolled Pt nanoparticles were consistently decorated on the CeO2-based nanoflakes using atomic layer deposition process to form a Pt/CeO₂ nano-array monolith catalyst. The catalyst exhibited good oxidation activity over singular gases of propylene and propane with ~90% conversion efficiency below 200°C.

Moving over to transition metal oxides, Choi et al. [73] prepared a new monolithtype oxidation catalyst made of titanium honeycomb substrates including an anodized TiO₂ surface covered with nano to micro pores and this was fabricated without a wash-coat layer and exposed to extreme flow rates of exhaust gas and engine vibration. The C₃H₆ conversion rates for the monolith catalyst were found to be as high as 90% around 170–180°C. Zhang et al. [74] synthesized a series of catalysts of which, Ru was supported by impregnation on a TiZr₂O₂/Graphene carrier prepared by hydrothermal method. The catalyst achieved 50% CO and C_3H_8 conversion at 125°C and 226°C, respectively. However, the main highlight is the use of graphene which is believed to have promoted the pore diameter and specific surface area of the catalyst, consequently augmenting uniform distribution of active sites and interactions between Ru and the composite oxide carrier. Characteristics of varied metal oxides and their composites are being tried and tested frequently for DOCs. Nevertheless, DOCs are not alone sufficient to mitigate soot as these only rid the soot particles from adsorbed volatiles to a certain degree. In order to completely rid the exhaust gas of soot, diesel exhaust systems are fitted with diesel particulate filters (DPFs), which will be discussed in the successive section.

9.3.2 Diesel particulate filters and catalyzed diesel particulate filters

Mitigation of soot precisely has seen low advancement hitherto. An effective method of soot elimination from engine exhaust is trapping it and passing the exhaust gas through a filter. A number of ceramic and metal-based DPF filters were developed and most efficient being a honeycomb monolith framework structure comprising of porous material, allowing soot to be trapped within these pores. The accumulation of particles within the filter leads to formation of a soot layer, which in a way increases filtration efficiency as the soot cake formed behaves like a sieve [75]. The consequential effect of this being increase of back-pressure toward the diesel engine thus decreasing its efficiency. Along these lines, the soot can be catalytically treated using diesel particulate filters (DPFs) with subsequent effective regeneration strategies for post combustion treatment. While a number of favorable catalysts have been proposed since the 1950s for soot elimination, it is indispensable to develop catalysts with a greater number of contact areas and enhanced reactivity to show impressive catalytic soot oxidation features. The combination of a DPF with an oxidation catalyst known as continuously regenerating particle trap (CRT) also known as catalyzed continuously regenerating trap (CCRT) are outstanding abatement systems. A schematic of which has been presented in Fig. 9.5B.

The soot oxidation process promoted by solid oxide catalysts ordinarily occurs via the Mars-Van Krevelen mechanism which is used to describe the kinetics of reactions such as selective oxidation of hydrocarbons based on the notion of cyclic reduction—oxidation reactions. The crucial steps involve supply of oxygen by metal oxide followed by introduction of oxygen species from the metal oxide into the carbon structure and the redox process concludes with the re-oxidation of the reduced solid catalyst by gas-phase oxygen present in air which assumes a steady state of RedOx reaction and is the rate-determining step. As can be observed in Fig. 9.5C the oxidation reaction process and the conversion of carbonaceous matter into CO_2 and H_2O occurs via chemisorption when the soot particles meet the metal particles on the catalyst surface. The diffusion of oxygen occurs on the surface of the catalyst occurs. The PAHs migrate to the surface of the catalyst and the oxygen present at this interface is activated and the oxidation process begins between the PAH and active oxygen species. Further, desorption occurs on the active sites of the reactional products [76–78]. In some measure another addition to this mechanism which is known to be operational involves the dissociative adsorption of di-oxygen on two adjacent active sites of noble metal catalysts such as Pt, followed by transfer of this oxygen from the active site to the surface of the support catalyst such as ceria or other transition metal catalysts having good OSC and exhibiting lattice oxygen mobility. This process is commonly known as "oxygen spillover." These activated oxygen species are liberated from the surface or lattice of the support catalyst and interact with the soot particles thus facilitating soot oxidation [79].

Innumerable catalysts have been inspected for soot emission control, i.e., PGM-based systems (platinum group metals such as Pd, Pt, Rh, and Ir) along with other materials like hydrotalcites, rare earth metals, mixed metal oxides of transition and inner-transition elements, spinels oxides and perovskites. In 1930, Roger K. Taylor studied the catalytic action of NaCl salt in the oxidation of carbon which was already being used as a hack in households to rid chimneys of soot. This study began after incidences of cancers were found more among chimney sweeps in areas where there was more soot. About 110 years earlier, Davy's [80] discovered that platinum wires could induce combustion of flammable mixtures without flames, inducing numerous experiments throughout the 19th century using various materials to carry out heterogeneous catalysis. Eugene J. Houdry developed and patented the first commercial oxidation catalyst called Oxycat in 1954. It was made up of two porcelain end plates holding in place 71 porcelain rods. These rods being coated with platinum and aluminum acting as a catalyst. The porcelain used was highly resistant to both thermal shock and mechanical stress. The rods were made in a tear-drop shape to ensure maximum catalyst surface and to minimize the resistance to the air flow directed through the oxycat. City air was passed through the catalyst after it was activated, the catalyst glowed red hot due to the exothermic reaction releasing carbon dioxide and water vapor [81].

Pure noble metals such as Pt and Pd sinter rapidly at diesel exhaust temperatures and hence need to be dispersed on inert supports such as γ -Al₂O₃, that can prevent sintering in practical applications as the atoms are dispersed preventing metal particle-to-particle contact and suppresses sintering [82]. Oi Uchisawa et al. [83] studied the differing effects of carbon oxidation with Pt with change in support catalysts and observed that Pt/SiO₂ showed greater activity as compared to Pt/Al₂O₃, which was closely related to enhanced Pt dispersion in SiO₂. The temperature of maximum reaction rate (T_p) along with synthesis methodologies have been briefly summarized in Table 9.2. Shuang et al. [86] prepared a Pt-Mg/Al₂O₃ catalyst exhibiting higher soot oxidation activity than the Mg-free catalyst. This effect was attributed toward the larger Pt particle size along with the synergistic effect between Mg and Pt which enhances the NO oxidation activity and enhances its storage capacity, thus, allowing an increased NO₂ production which being a

Catalyst [Ref.]	Synthesis method	Conversion temperatures
1% Pt/SiO ₂ [83]	Incipient wetness method	$T_{p} (1\%/Pt/SiO_{2}) = 312^{\circ}C$
$1\% \text{ Pt/Al}_2\text{O}_3$		$T_{p} (1\%/Al_{2}O_{3}) = 460^{\circ}C$
Pt/Ta ₂ O ₅ [84]	Incipient wetness method	$T_p = 350^\circ C$
1%/Pt/SiO ₂ [85]	Incipient wetness method	$T_{p} (1\% Pt/SiO_{2}) = 562^{\circ}C$
V ₂ O ₅ -Pt/SiO ₂		$T_{p} (V_{2}O_{5}-Pt/SiO_{2}) = 518^{\circ}C$
MoO ₃ -Pt/SiO ₂		$T_p (MoO_3 - Pt/SiO_2) = 475^{\circ}C$
Pt/Al ₂ O ₃ [86]	Incipient wetness method	$T_p (Pt/Al_2O_3) = \sim 439^\circ C$
$Pt-Mg/Al_2O_3$		$T_p (Pt-Mg/Al_2O_3) = \sim 432^\circ C$
Au/SiO ₂ [87]	Incipient wetness method	$T_p (Au/SiO_2) = \sim 300^\circ C$
Cu/SiO ₂		$T_p (Cu/SiO_2) = \sim 260^\circ C$
Ag/SiO ₂		$T_p (Ag/SiO_2) = \sim 200^\circ C$
$Au - V_2O_5 / TiO_2$ [88]	Incipient wetness method	$T_{p} (V_{2}O_{5}/TiO_{2}) = 445^{\circ}C$
		$T_{p} (Au - V_2O_5 / TiO_2) = 419^{\circ}C$
CeO ₂ [89]	Co-precipitation method	$T_{p} (CeO_{2}) = 518^{\circ}C$
ZrO_2		$T_{p} (ZrO_{2}) = 582^{\circ}C$
CeZrO ₂		$T_p (CeZrO_2) = 521^\circ C$
CeO_2 [90]	Combustion followed by	T_p (Uncat. soot) = 528°C
CeLaO	wetness impregnation	$T_{p} (CeO_{2}) = 474^{\circ}C$
CePrO		T_p (CeLaO) = 460°C
CeSmO		$T_p (CePrO) = 419^{\circ}C$
CeYO		T_p (CeSmO) = 493°C
		T_p (CeLaO) = 504°C
CeO ₂ [91]	Co-precipitation method	$T_{p} (CeO_{2}) = 555^{\circ}C$
La–Ce oxide		T_p (La-Ce oxide) = 535°C
Nd–Ce oxide		T_p (Nd-Ce oxide) = 569°C
Mn–Ce oxide		T_p (Mn-Ce oxide) = 475°C
Fe-Ce oxide		T_p (Fe-Ce oxide) = 480°C
Cu–Ce oxide		T_p (Cu-Ce oxide) = 430°C
CeO_2 [92]	Combustion followed by	$T_{\rm p} ({\rm CeO}_2) = 3/8^{\circ}{\rm C}$
Ag/CeO_2	wetness impregnation	$I_{p} (Ag/CeO_{2}) = 332^{\circ}C$
Au/CeO_2		$I_p (Au/CeO_2) = 366^{\circ}C$
Pd/CeO_2		$I_p (Pd/CeO_2) = 3/3^{\circ}C$
Pt/CeO_2		$I_p (Pt/CeO_2) = 34/C$
Rn/CeO_2		$I_p (Rn/CeO_2) = 514 C$
Pt/Al_2O_3	Co-precipitation method	$I_p (Pt/Al_2O_3) = 3/8 C$ T (C ₂ O ₂) = 378°C
(commercial) [93]		$I_p (CeO_2) = 3/8 C$
CeO_2		$T_{p} (Win_{2}O_{3}) = 578 \text{ C}$ T (MaCaO) = 378°C
Mn_2O_3		$I_p (WIIICeO_x) = 578 C$
C_{2}	EDTA citrate method	T (Uppert sect) $= 500^{\circ}$ C
$C_2 H f_2 [94]$	EDTA-citrate method	T_p (Oncat. soot) = 500°C
C_{2}		$T_p (CeO_2) = 508 C$ T (CeHfO) = 443°C
C_2		T_p (Cerrifo ₂) = 445 C T_ (CollfThO) = 418°C
$CeHfPrO_{2}$		$T_{p} (CeHfSmO_{2}) = 410 C$
CeHfl 2O2		T_p (CeHfNdO ₂) = 436°C
CG IILaC 2		$T_{p} (CeHfPrO_{2}) = 389^{\circ}C$
		T_{p} (CeHfI $_{2}O_{2}$) - 404°C

 Table 9.2 Comparison of activities of metal oxides as soot mitigation catalysts.

great oxidizer efficiently promotes soot ignition. Hence, on scrutinizing the above characteristics of PGM oxide catalysts one can comprehend that the objective is to employ the porous walls and large surface area of the DPF substrate as a support for a thin coat of catalyst without allowing any major decrease in pore size. PGM oxides have high activity and are quiet versatile, however, due to high cost replacing these with cheaper active phase catalysts is now a necessity.

Nonplatinum metals such as Au, Ag, and Pd have not been as frequently investigated, although recent literature contains a number of articles on the use of Ag and Au. Cooro et al. [87] impregnated Ag, Au, and Cu on SiO₂ and on comparing activities, they found Ag/SiO_2 as a potent catalyst due to its ability to easily form several suboxide species in oxidation atmosphere. The electron transfer from the metal to O_2 leading to chemisorption of oxygen on metal surface is dependent upon the ionization energy of the metal. Nevertheless, Au cannot generate adsorbed atomic oxygen species at its periphery due to difficulty in transferring electrons from Au⁰ to O₂. Similarly Cu converts to Cu₂O effortlessly leading to strong deactivation of the catalyst. Ceria-based catalysts are promising contenders, they store oxygen amid the reduction process and release oxygen amid oxidation because of its ability to switchover between Ce⁴⁺ and Ce³⁺ oxidation states [95,96]. However, thermal aging leads to significant deactivation of the catalyst. It is also worth noting that the temperature in the interior of a DPF can increase up to $\sim 1000^{\circ}$ C and even higher in specific regions as the oxidation process is highly exothermic. Ceria has a high risk of sintering leading to loss of metal surface area and it is only conceivable that loss of metal surface area leads to monotonic decrease in activity and losing its catalytic properties including its oxygen storage release (OSR) capacity. At the same time, fuel-derived sulfur and lubricant-derived phosphorous has potential to severely poison the catalyst and eventually diminish catalytic activity [97,98]. Accordingly, the research activities have been primarily fixated upon improvement of the surface area, stability in CeO₂ using a promoter.

Atribak et al. [89] recounted that the catalytic soot combustion of CeO_2 can be significantly improved by Zr doping as it enhances thermal stability of CeO_2 , while maintaining its activity and selectivity for CO_2 . Rare-earth remodeled CeO_2 were studied for soot oxidation and doping with Pr and La showed a decrease in oxidation temperature by almost 100°C while doping with Sm and Y exhibited lower activity than CeO_2 itself. The NO_x generated over these catalysts through the reaction of NO with lattice oxygen is responsible for the decrease in the soot oxidation temperature. However, due to low abundance of rare-earth elements such catalysts are not commercially viable. On comparing the addition of Ln and transition metals to CeO_2 , Muroyama et al. [91] resolved that although addition of Ln oxides increases thermal strength and consequently the surface area, however, no remarkable improvement of catalytic activity was established. On the contrary, addition of transition metal oxides significantly promoted soot oxidation. This could well be a result of enhanced RedOx capabilities of transition

elements. The dispersal of noble metals on CeO₂ was exemplified by Lee et al. [92], in which Ag and Au showed less dispersion over the support catalyst and the Au particles appeared significantly larger and sintered. Rh greatly promoted vacancy formation and hence enhanced oxygen adsorption thus bettering the redox property of CeO₂. NO is oxidized over catalysts to NO₂ and at elevated temperatures, nitrates decompose liberating NO₂ to the gas phase which acts as the oxidizing medium for soot. The nitrate storage capacity of MnCeO_x is three to five folds greater than that of singular oxides resulting in a contribution of the released NO₂ to the soot oxidation process. This strong synergistic effect of manganese and cerium is reported by Tikhomirov et al. [93] on the soot oxidation. Harshini et al. [94] prepared ceria-hafnia solid solutions and further doped these with trivalent rare earth elements. It was observed that these ions can replace Ce⁴⁺ ion to generate an oxygen valency by charge balancing and utilization of such Ln ions, consequently increasing the OSC of the catalyst.

A number of other metallic compounds in the form of single or mixed transition metal oxides have extensive prospects by their nature to behave as effective catalysts. However, they face a handful of shortcomings such as insufficient redox sites, thermal instability, deactivation by catalytic poisons, ineffective regeneration, etc. Reciprocity among different metal combinations, modifying the nanostructured morphology along with surface and internal defect engineering, can significantly enhance and optimize catalyst activity. Transition metals that can accomplish redox cycles of varied nanostructural dimensions and porosities have already been extensively researched. Catalysts such as TiO₂ [99,100], ZrO₂ [101–103], WO₃ [104–106], MoO₃ [107], MnO₂ [108,109], NiO [110], spinels [111,112], perovskites [113–115], etc., have been used for varied catalytic applications and may also have high potential toward soot oxidation. In particular, the mixed oxides of these metals exhibit wide variety of electronic and chemical properties making them intriguing materials for research and technological applications alike, however, touching upon all these is out of the scope of this chapter. The bottom-line is that for enhanced soot oxidation activity, the catalyst should possess remarkable OSR capabilities along with thermal stability which includes resistance to sintering and at the same time it should be sufficiently resistant to catalyst poisons such as fuel derived and lubricant derived sulfur, phosphorous, etc.

9.3.3 Fuel-borne catalyst-assisted soot depletion

The performance of DPF filters formerly deteriorated due to insufficient regeneration, durability, and steadfastness. Hence, fuel-borne catalysts (FBCs) were implemented to enhance the overall after-treatment performance. Addition of a suitable FBC to diesel fuel could not only augment regeneration capabilities but can alter physicochemical properties of soot and essentially decrease its oxidation temperature [116]. The most commonly researched FBC are cerium and iron nanoparticles and their composites. Cerium has several advantages such as easy valence state transformation, high OSC

and great thermal properties, as compiled by Hoang et al. [117]. CeO₂ nanoparticles with size <100 nm when used with diesels and biodiesel blends enhance combustion and promote soot oxidation. It was also concluded that ceria used as an FBC improved engine performance for diesel engines fueled with biodiesels. The primary fuels blended with nanoparticles simply known as *nanofuels* are synthesized by vapor deposition, laser ablation, submerged arc synthesis, ultrasonication, magnetic stirring, pH adjustment, etc. One or more of these techniques might be employed to achieve homogeneous dispersion. The exact mechanism of action is not yet understood, however, it has been speculated that it could be possible that oxygen vacancies in the metal oxide are swiftly filled with gaseous oxygen and transferred to soot promoting oxidation [118,119]. Yet other researchers claim that emission reduction could be a consequence of water from fuels reacting with hydroxyl radicals formed during reactions with the nanocatalysts and their further reaction with carbon atoms thereby lowering oxidation temperatures [120].

Iron-based FBC have also shown promising possibilities due to their easy solubility in diesel fuels, cost-effectiveness, thermal stability, and are safe to handle. Nash et al. [121] suggested iron-based additives reduced particle mass and volume along with reducing black carbon emissions by 30%—40% during soot oxidation, but on the other hand particle number concentrations heightened by about five folds. Fe in the form of ferrocene when added to a combustion mixture lowered flame temperature which obstructed the growth of small PAHs into bigger ones by reacting with oxygen and hydroxyl radicals [122]. In this method the fuel requires to be dosed with the catalyst and this leads to certain disadvantages such as addition of catalyst at refinery stage would require an appropriate grade of the fuel along with modifications in refining processes. If the catalyst is added later during fueling, maintaining certain protocols would require expertise in dosing methods and for on-board delivery systems, the supply of catalyst would require to be adequate in order to avoid excessive dosing [123]. In certain instances it was found that metal ions present in fuels also make their way into soot particles and can eventually be fatal to the environment [12].

9.3.4 Novel additives and fuel blend formulations

In order to overcome the above-mentioned complications of FBC addition, addition of liquid additives to fuel have been known not only to reduce pollutant emissions but also to enhance combustion processes. Biodiesels being renewable, sustainable, nontoxic, and in most cases originating from waste materials have been an excellent diesel additive and their addition does not require major modifications of present day engine systems for smooth functioning. Biodiesel also backs up the Renewable Fuel Standard (RFS) program, working toward the reduction of greenhouse gas emissions and expansion of the renewable fuels sector simultaneously reducing reliability on fossil fuels. They comprise of a complex combination of fatty acid methyl esters (FAME), which are usually a product of esterification of vegetable and seed oils, waste vegetable, and animal fats on

reacting these with monohydric alcohol in presence of a catalyst to form a corresponding monoalkyl ester [124]. The investigational variables in such a synthesis include reaction time, catalyst concentration, and oil-to-methanol molar ratios. The composition of the FAME product can be analyzed using gas chromatography and other physicochemical characterization techniques.

Morajkar et al. [12,15,42] and Abdrabou et al. [49], and along with many other researchers have investigated the consequences of adding biofuels such as karanja, palm oil [125], Camphor oil, sunflower oil [126], jatropha, rapeseed oil [127], etc., to diesel and their resultant repercussions on soot nanostructure and oxidative reactivity. The addition of these additives results in increased structural disorder, decreased primary particle size, and higher percentages of oxygen functionalities in the soot structure. A higher degree of disorder in the soot nanostructure results in higher possibilities of an attack by O_2 and other radicals such as hydroxy radical during the combustion process. In Fig. 9.3A, the highest intensity curve in the XRD plot indicated by a black line corresponds to diesel soot while the others belong to Jatropha biodiesel blended diesel soot under different experimental conditions which show relative extensive broadening and lower intensity of peaks indicative of excessive crystal disorder due to random PAH stacking orientations. Similarly the activation energy required during soot oxidation is lower for oxygenated fuels as seen in Fig. 9.4C.

These vegetable oil—based biodiesels have their characteristics of viscosity, flash point, cetane number very close to petroleum diesel, and can be used in diesel engines with little to no modifications. However, the viscosity of vegetable oil is several times higher than that of mineral diesel owing to its large molecular mass and chemical structure. This leads to unfavorable pumping and sprays characteristics. As a result, these oils can cause poor fuel atomization, partial combustion, and carbon depositions on the injector and other engine parts resulting in serious mechanical fouling. Common methods to avoid this include blending with diesel, microemulsification, thermal cracking, and transesterification [128,129].

9.3.5 Low-temperature combustion strategies

Differing technologies are being tried and tested for soot emission abatement, in-cylinder reduction techniques, such as Low-Temperature Combustion (LTC) are the bottom-line in research and development of state-of-the-art diesel engines. These engines reduce operating temperatures either by increasing Exhaust Gas Recirculation (EGR) or by operating in excess air ratio higher than 1, i.e., leaner mixtures. The exorbitant cost of fossil fuels and their lack of availability concludes that the future is dependent on alternative renewable fuels. Varied physical and chemical characteristics of petroleum diesel and biodiesels result in differing emission characteristics as discussed previously. LTC is a general term of the unification of Homogeneous Charge Compression Ignition (HCCI) combustion, Premixed Charge Compression Ignition (PCCI) combustion and

Reactivity Controlled Compression Ignition (RCCI) combustion, etc. [130]. LTC strategies decrease NO_x and soot simultaneously but increase HC and CO emissions, however, focusing on PAHs, i.e., soot precursors coagulate at sufficiently high temperatures (~1500°C) and in rich mixture zones to form soot particles. The soot oxidation process has higher sensitivity toward temperature comparative to the soot formation process, consequently on application of EGR the combustion temperature drops and oxidation rate falls dramatically. In low temperature systems, oxidation of PAHs to CO and CO_x is hundred-to-one, but the coagulation of PAHs to initiate soot formation does not occur at LTC temperature ranges. Therefore, LTC modes successfully help accomplish soot reduction which is sometimes a major concern in the use of diesel fuels [131,132].

Traditional engines release UHCs through exhaust gas, these are formed from trapping of fuel in crevices of the combustion chamber during over-lean or over-rich fuel mixtures and incomplete evaporation of this fuel. In case of overly lean mixtures, the fuel cannot propagate through the mixture efficiently and partially oxidized fuel pyrolysis leads to formation of UHC and CO. Whereas in overly rich fuel mixtures fuel does not mix efficiently with air and evenly enough to get oxidized intensively, resulting in formation of UHCs and CO. The LTC system comes with its own set of drawbacks which also require meticulous scrutiny. The reduction in in-cylinder combustion temperature, overly lean mixtures, rapid combustion, and reduced oxygen concentration increase concentrations of unburnt hydrocarbons (UHC) and CO [133-136]. HC emissions are primarily dependent upon ignition delay, whereas CO emissions depend upon equivalence ratios. The use of biodiesels is known to reduce UHC and CO emissions and increase NO_x emissions which is contrary to the emission characteristics of LTC modes. On these grounds, it could be concluded that using biodiesels or their blends in LTC engines could remarkably reduce overall pollutant emissions and could be the most reliable engine and fuel system for future applications.

9.4 Summary and conclusion

In a nutshell, this chapter features the remediation techniques to curb pollution resulting from soot. In this regard, the physicochemical properties, formation, and nanostructure along with size distribution and the various characterization techniques involved in soot analysis were effectively discussed. At the same time prior to highlighting the soot abatement processes, the biological toxicity of this malignant pollutant were also discussed. Catalytic convertors and diesel oxidation catalysts used in gasoline and diesel vehicles, respectively, are effective in converting adsorbed species and organic volatiles into less harmful products. Although a robust system such as a continuously regenerating particle trap (CRT) has to be in place in order to effectively convert soot into CO_2 and H_2O and cause minimal environmental and health damage. But, in spite of placing DOCs and DPFs in the exhaust after-treatment system, due to lack of regeneration or poor functionality, soot particles escape into the atmosphere. In order to curb this, fuel-borne catalysts are added to the fuel prior to combustion to enhance oxidative reactivity internally and facilitate cleaner combustion. However, this comes at a risk of increasing nanoparticle emissions into the environment through exhaust and hence needs proper monitoring. In order to provide greater environmental sustainability, renewable biodiesels are being put into use which not only reduce the burden over fossil fuels but also enhance combustion efficiency and reduce pollutants. Being oxygenated, they result in lesser soot formation and also decreases the burden on DPF filters. Last but not the least, the LTC mode of operation was reviewed, wherein, the engine is adequately modified to promote exhaust gas recirculation which helps accomplish soot reduction. All these techniques have their own advantages and drawbacks. While one overcomes the limitations of another it comes in with its own new set of constraints. The present research focuses on curbing these constraints by using multiple techniques in combination to develop an optimum process that can not only limit pollutants but diminish them to negligible levels.

9.5 Challenges and future outlook

Modernization and industrial revolutions elevated our living standards at the cost of degrading the environment and now it is the need of the hour to curb activities that have fatalistic consequences. Numerous techniques are being used to minimize pollution due to soot and novel methods are being continuously developed. However, reconditioning the existing techniques with suitable alterations could lead to greater outcomes. Regenerating DPF filters have been quiet successful in reducing soot, however, due to catalytic limitations such as activity and stability, the practical application has been limited. A catalyst with greater surface area and OSR capacity along with resistance to poisons such as sulfur, phosphorous, and moisture is highly favorable. The catalyst should be an oxidizing catalyst and a reducible oxide with a high thermal threshold. Such properties were noticed in transition metal atoms, however, in recent studies it has been observed that synthesis conditions and morphological alterations using distinct surface directing agents can not only enhance performance of transition metals as catalysts but also allows the use of metalloids and other p-block elements which can be appropriately modified to suit the catalytic preferences with fewer toxicological effects and metal deposition complications. Similar properties of catalysts are required for use as FBCs, although understanding the renewability of these and their sustainability in combustion environment is a concern. Moving over to fuel additives, biodiesels and other oxygenated additives are highly efficient although they are known to consequently increase NO_x emissions which can be further reduced by incorporating these with LTC modes. Thus, from all the above discussions it can be deduced that to an extent we already possess the necessary solutions, further modifications, and enhancement of existing processes

from laboratory scale to technology readiness level 6 or above is needed to achieve effective practical remediation of combustion generated soot from the environment.

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