Asian Journal of Chemistry Vol. 20, No. 8 (2008), 5797-5817

REVIEW

Fuel Additives for Particulate Matter/Dust Reduction

D.C. KIM, K.C. SONG† and R.D. KAUSHIK*‡
Alternative Fuel Research Center, Fossil Energy and Environment Research Department
Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea
E-mail: rduttkaushik@yahoo.co.in

This review covers the recent reports related to the recent developments in the field of application of various types of fuel additives for reduction of particulate matter/dust in exhaust gases resulting from incomplete combustion of hydrocarbon fuels. Different aspects of these emissions like the concern about polycyclic aromatic hydrocarbons adsorbed on soot particles, the trade-off between PM and NOx emission, *etc.* are presented. The metallic, organometallic and non-metallic additives including oxygenates, nitrogenates and nitro-oxygenates have been described in reference to various types of fuels like heavy fuel oil, diesel, mixed fuels, biodiesels and gaseous fuels. Progress made in deciding the probable mode of action of these additives has also been incorporated.

Key Words: PM/Dust reduction, Metallic and non-metallic additives, Different fuels.

INTRODUCTION

Particulate matter (PM) is a general term describing small particles in the ambient air, such as dust, marine-derived particles, liquid droplets, smog components and soot. PM in exhaust gases from combustion facilities is called as dust. Soot consists of small PM particles, amorphous carbon and polycyclic aromatic hydrocarbons (PAH). Soot becomes a part of black carbon/smoke when present in sufficient particle size and quantity in exhaust gases resulting from incomplete combustion of hydrocarbon fuels. $PM_{2.5}$ is a term used for PM having particle size less than 2.5 μm that constitute a significant portion of soot and are able to affect the deeper parts of lungs leading to asthma, chronic bronchitis and heart diseases[1]. Black carbon originating from combustion processes, scatters and absorbs the incoming solar radiations, contributes to poor air quality and induces respiratory and cardiovascular problems[2]. In outdoor air, diesel particulates contribute to the total concentration of total suspended particulates. All diesel particulates can be classified[3] as PM_{10}.

†Department of Chemical Engineering, Konyang University, Nonsan, Republic of Korea.
‡Permanent address: Department of Chemistry, Gurukul Kangri University, Haridwar-249 404, India.

Because small particles like those under PM_{10}, are capable of penetrating the filtering mechanism of the respiratory tract and can be deposited in the bronchi or lung tissue, aerosols stemming from combustion processes are unwanted particularly in the areas where they can be inhaled by humans. Medical studies[4] have shown that non-volatile ultrafine particles with diameter < 100 nm, can cause inflammation and respiratory diseases and the effect depends upon the surface area of inhaled particles and not on the particle mass. These particles can adsorb the hazardous substances and transport them into human organism. PAH are such typical adsorbates from combustion sources and many of these are carcinogenic[5,6]. The ultrafine particles reduce visibility[7] and may influence the climate related effects like cloud formation[7]. The origin, activity and concern about PAH have been presented very well in a review article that has reported recently[6]. The probable carcinogenic PAH are[6], chrysene ($C_{18}H_{22}$), benzo[a]anthracene ($C_{18}H_{12}$), benzo[b]fluoranthene ($C_{20}H_{12}$), benzo[a]pyrene ($C_{20}H_{12}$), dibenz-[a,h]anthracene ($C_{22}H_{14}$) and indeno[1,2,3-c,d]pyrene ($C_{22}H_{12}$), *etc*.

Environmental legislations are becoming increasingly restrictive over emission limits[8-10]. Moreover, the need for fuel savings is also an objective of power producers for both economic and environmental reasons. The meeting of both of these targets is often difficult and it becomes more difficult in case of low quality of fuel especially in terms of stability. Johnson[11] has reviewed the recent developments in regulations to limit diesel emissions, diesel technology and remediation of NOx and PM. Neeft *et al.*[3] mentioned the typical combustion PM emissions g/Kg of fuel as 0, 1, 0.05-2, 0.05-0.5, 1-20, 1-10, 0.1-0.4 and 0.05-0.3 for power generation by natural gas, heavy residual oil, coal, municipal waste combustion, wood or coal open fires/stoves, diesel engines, otto engines and otto engines using 3-way catalyst (although the data depend on the process and fuel specification).

Soot emission in any combustion process is indicative of inefficient combustion and leads to poor thermal efficiency. The emissions depend upon the burner type and quality of fuel used. Przybilla *et al.*[12], studied the effect of burner type [Giersch (Y) yellow flame standard extra light oil burner, Weishaupt (Y-R) yellow flame extra light oil burner equipped with flue gas circulation system (for improving soot and NOx) and MAN (B) blue flame extra light oil burners] and fuel on ultrafine particle emissions of residential oil burners. A study[13] on influence of atomization quality, burner aerodynamics, air staging, reburning using methane and propane as secondary fuels and fuel atomization using mixtures of air and methane on pollutant emissions revealed that burner operating conditions that can procure both low NOx and PM emissions are extremely difficult to achieve. Further, reburning reduces the NOx but its effect on PM is beneficial only if propane is used as secondary fuel. Also the fuel optimization using mixtures of air

and methane can be useful for simultaneous reduction of NOx and PM. The trade-off between PM and NOx emission should be avoided and it requires complex methodology[14]. Therefore, such fuel additives are required that can reduce PM without affecting NOx emission[15].

However, the combustion efficiency can be improved only up to definite limits by using properly designed burners, their accurate control and using good quality fuel. Once the plant is optimized, the only way to improve the combustion efficiency and to reduce particulate emissions is to inject a chemical additive. The chemical techniques that are available these days and have found industrial acceptance for reducing the particulate emissions, are either based on utilization of water in oil emulsions that create a secondary atomization or on using the combustion catalysts which improve the rate of oxidation of soot particles.

A well accepted theory for particulate formation during combustion processes postulates that combustion takes place from the outer to inner layer of fuel droplet. Fuel droplet is pyrolyzed and submitted to chemical change. Further, the fuel droplet becomes highly viscous and forms a shell that is capable of trapping the gases. It results in an increase in the internal pressure and swelling of droplet. Besides the formation of cenospheres, a number of solid soot particles are expelled during the boiling of trapped gases[16]. Soot formation takes place in three stages, soot particle nucleation, formation of spherical units of about 250 Å size by agglomeration and surface growth and coagulation of these particles to form the specific chain like structures[17].

Soot formation takes place at high temperature, in fuel rich zone around fuel droplets where hydrocarbons undergo oxidation limited by oxygen concentration. When oxygen is transported by diffusion through the flame front, it is called as diffusion flame and when premixed amount of air and fuel is combusted, it is called as premixed flame. The later has higher temperatures than the former. The formation of soot is assumed to proceed *via* the elemental steps, like pyrolysis, nucleation, surface growth and coagulation, aggregation and oxidation. These processes take time from microseconds (initial nucleation step) to milliseconds (completion of soot formation, oxidation and cooling by cylinder expansion in diesel engines)[3].

Bacharach soot number[18] is a qualitative measure for evaluating the completeness of combustion based on the optical absorption of emitted particles deposited on a filter. A well defined amount of flue gas is sucked through a white filter leaving behind a discoloured spot whose colour is compared with a defined gray scale ranging from 0 (white) to 9 (black). This number is assessed electronically by measuring the reflectance of visible light on the loaded filter. The discolouring of sample filter is attributed to the presence of soot, which is assumed to be composed mainly of elemental

carbon. Deposited organic residue like unburned fuel may also decolourize the filter and lead to some misinterpretation of the obtained Bacharach soot number. This number should not exceed 0.5 for residential extra light oil burners[19].

The attempt of reducing the emissions from combustion processes is often assisted by the use of fuel additives. These additives, when used in appropriate amount, serve the purpose of catalyzing the combustion process and reducing the amount of emitted soot particles. As an alternative to Pb and Mn based additives that are not safe from human health view point, the Li, Na, K, Cs, Ca, Sr, Ba and Fe based additives have been explored. Howard and Kausch[17] have extensively reviewed the knowledge available up to the year 1980 and noted that Ba, Fe and Mn additives are most effective out of which, the Fe additives are safer to use. Two comprehensive reviews[3,20] on the process of soot formation and diesel particulate emission control have also appeared after that. In the present article, an attempt has been made to up-date the knowledge related to the various types of fuel additives generally employed for PM/ dust reduction.

HEAVY FUEL OIL ADDITIVES

Heavy fuel oil which is used for steam production in power stations *etc.*, is produced from crude oil by blending the heavy liquid residues (which remain after the removal of valuable oil fractions), with heavy distillate oil. Its use in boilers causes loss of boiler availability due to the external fouling and corrosion of the high temperature and low temperature heat exchange surfaces. It leads to slagging in combustion chamber, the formation of bonded deposits on high temperature surfaces, corrosion and blockage of air heaters and other ancillary equipment operating at lower temperatures, formation of carbon residues and NOx[21].

Use of fuel oil additives has many advantages like improvement in boiler availability and cleaning requirements (as deposits are soft, friable, non-corrosive and easy to remove), elimination of high temperature corrosion and tube wastage, reduction in fuel consumption and reduction in SO_3, NOx, dust and acid smut emission. In addition, they increase the potential to handle a lower grade heavy fuel oil having high contents of ashpaltenes, V and Na[22]. Ferrara[16] reported the impact of a chemical additive on sludge formation and PM reduction during fuel oil combustion in power station boilers. The additive contained asphaltenes stabilizers patented by MEG (Italy) and prevented the asphaltenes aggregation and precipitation. 500 ppm dosage of the additive, freed the fuel tank from 50 cm sludge and PM was reduced to 18 mg/Nm^3 from 50-60 mg/Nm^3 in flue gas.

The metals manganese, iron and barium are most often reported to be highly effective in this regard, although the problems of metal oxide deposits on combustor surface sometimes prohibit their use[17]. Manganese usually

converts into MnO, MnO_2, Mn_2O_3 or Mn_3O_4 as combustion products in boilers and gas turbines, the amount of these oxides being dependent on the temperature of the process[23-27]. High atmospheric concentration of these oxides results in chronic manganese poisoning, manganic pneumonia and catalytic oxidation of other air pollutants to undesirable products[28]. A part of the barium emission is in the form of water soluble barium compounds that are usually toxic[17,29]. Iron additives and their combustion products are safest of these three metals[17]. The widely used Fe compound, ferrocene, has been explored extensively in animal feeding studies which show almost absence of toxicity although high concentration of iron oxides can cause irritation[30].

Ferrocene or dicyclopentadienyl iron ($Fe(C_5H_5)_2$) has been found to be the most effective PM reduction additive in oil-fired combustors in the utility and domestic boilers, in comparison to naphthenates of Ni, Co, Mn, Pb and Mg[31]. Ferrocene is also known for its thermal stability upto about 500 ºC and therefore, it may not have catalytic effect in some flames except in high temperature zones[32].

An iron chelate in large concentrations of 0.01-0.08 % (w/w) in fuel has been reported to be more effective than 0.05 % hydrazine[33,34] or copper sulphonate[35]. Transition metal complexes having 20 % Fe and 25 % Mn were found to be most effective for PM reduction in oil fired domestic boilers[17]. Seven most effective additives based on Fe, Mn, Ca and Co were found by Martin *et al.*[36] to cause 53-69 % PM reduction in residential oil-fired burners used for domestic boilers. Many flame parameters like flame type, burner design, fuel equivalence ratio, flame temperature, type of fuel and the smoke evaluation technique also have significant influence on the effect of additives used for PM reduction[17]. Methylcyclopentadienyl manganese tricarbonal (MMT) has been found to be good PM reduction agent in boilers[23], although it increases the PM in cleaner combustors[24] and toxicity of its combustion products (various oxides of Mn) is still controversial[23-25].

Recently[12], the addition of ferrocene has been reported to reduce 100 nm soot particles in residential oil burners generating at the same time, 25 nm iron oxide particles. It happened when a mistuned burner with Bacharach number of 4.5 was employed and the soot emission by far exceeded the legal limits. Even at low additive concentration, the formation of iron oxide particles led to significant increase in total particles. In case of well adjusted burner (Bacharach number ≤ 0.5), the lack of soot formation makes the formation of small iron oxide particles dominant upon addition of ferrocene. Lighty *et al.*[37] feared that the use of iron based fuel additives may be counter-productive with respect to health effects.

Witzel *et al.*[12] reported the PM reduction by four organometallic additives based on Ce, Fe and Ca for heavy fuel oil combustion and found that 90

ppm Fe concentration caused 29 and 62 % PM reduction in presence of two organometallic compounds (exact structure not given) in 1.16 MW boiler. They concluded that metal makes the cenosphere more reactive by promoting the heterogeneous surface reaction and lowering the ignition temperature. Further, by lowering the ignition temperature, it allowes more time for the cenosphere to burn towards the end of the combustion chamber. The role of organic part of the organometallic compound is to retain the metal within the cenosphere and thus, making it more effective.

If MgO based additive is injected in the lower section of furnace or direct to heavy fuel oil, a light reflective coating of MgO, known as white effect, may be formed on the furnace tubes[38]. Davini and Tartarelli[29] studied the effect of particle size of MgO additive to heavy fuel oil using two different capacity burners. They found that SO_3 and NOx reduction increases at greater surface area of MgO particles while low surface area of the same causes soot less acid formation. A report[40] on the cost benefit analysis for eleven heavy fuel oil additives based on MgO, Mg, Fe and some catalysts showed that the cost of using these additives ranges from 0.3 % of fuel cost at full load to 0.6 % at 50 % load assuming a constant injection rate. Operational problem may occur while using the MgO additives by front end injection technique due to the white effect[40].

Kim *et al.*[29,41] reported the preparation of some Fe-nanofluids containing $Fe(OH)_2$, $Fe(OH)_3$ and Fe_3O_4 in diesel starting from industrial waste containing $FeSO_4{\cdot}7H_2O$ as the precursors for NOx and dust reduction in heavy fuel oil-fired boiler facilities. They also reported the results of PM reduction by $Fe(OH)_3$ nonofluid in heavy fuel oil-fired combustion boilers under constant condition of 4 % O_2 in flue gas[42]. An improved efficiency was expected as in the combustion furnace, $Fe(OH)_3$ is expected to convert into Fe_2O_3 in combustion facilities[32] where the temperature generally lies[20] between 1500-2500 K. This Fe_2O_3 is effective for PM reduction as reported by earlier workers too[17]. Further improvement in its action is expected when it is added in the form of nanofluids as an increase in surface area will felicitate the occlusion of metal in to soot particles accelerating thereby the rate of oxidation of soot in O_2 rich flame zones[43]. The additive investigated has been claimed to be simple to prepare, involves less cost of preparation (as the industrial waste low cost iron sulphate was used for preparation of Fe-nanofluid) and simple mode of operation. Addition of this Fe-nanofluid did not bring any significant change in CO, SOx and NOx contents of flue gas. The PM reduction was optimum (53.3 %) on addition of active metal concentration of 100 ppm. An explanation for insignificant effect of additive on NOx reduction and the probable reactions involved during PM reduction were also put forward by them[42].

DIESEL ADDITIVES

Diesel particulates are defined by USEPA[3] as 'all compounds collected on a pre-conditioned filter in diluted diesel exhaust gases at a maximum temperature of 325K'. These particulates consist of soot nuclei (carbon) including inorganic material, adsorbed hydrocarbons (or soluble organic fraction), SO_3 (or sulphuric acid) and little water. The size of individual soot sphere[3] is about 25 nm and that of total particle is about 200 nm.

For elimination of emission of soot from diesel vehicles, it is a general practice to trap the particles on specific filters like SiC filter, followed by periodic oxidative regenerations to prevent a pressure increase in the exhaust line. For decreasing the temperature of the regeneration process significantly to protect the engine filter, organometallic compounds can be added to fuel[44]. Fuel additives are added to fuel in order to improve diesel engine efficiency, reduce emissions or, if regenerative particle traps are used, to assist the regeneration process. Usually, additive is added as oregano-metallic compound and found in emissions as oxide.

Metallic additives: Matter and Siegmann[45] found that total carbon shows an over proportional decrease while total PM is reduced only slightly on addition of/seeding with 120 mg ferrocene/Kg diesel fuel in the emission of heavy duty diesel engines. It was attributed to the addition of iron oxide nuclei from the seeding to PM due to which the mass of these nuclei happens to almost compensate the reduction of carbonaceous matter which is generated by the fuel additive. On the other hand the additive was concluded as effective since it reduced total carbon as expected.

For the same type of diesel engines, Kasper *et al.*[46], on the basis of particle size resolved aerosol photoemission, reported the formation of condensation nuclei of iron oxide in combustion zone prior to the formation of carbonaceous particles in methane and acetylene diffused flames. In methane flame, ferrocene reduced carbonaceous matter in combustion by more efficient burnout rather than by inhibition of soot formation and it led to formation of iron oxide particulates early in flame *i.e.* below soot inception point of a flame not seeded with iron oxide. In acetylene diffusion flame, iron oxide was incorporated in the soot particles and catalyzed the soot burnout at tip of the flame. Above the flame, the iron oxide particles reappear in exhaust.

Burtscher *et al.*[47-51] used scanning mobility particle sizer (SMPS), gravimetric, coulometric and ICP-MS analysis to find that certain amount of additive material (ferrocene and Ce compounds) can be incorporated in the soot particles and if this limit exceeds, the formation of new ultrafine particles (having only the additive material) starts whereas the additive contributes only little to the larger soot particles. Thus, if the additive concentration is increased beyond the onset of particle formation, no further decrease in soot emissions is observed. From this point of view, an additive dosage just at the limit of particle formation seems to be optimal.

In diesel fuelled vehicle engines, organometallic compounds based on Cu, Mn and Ce have been shown to decrease ignition temperature of particulate matter from 550-600 ºC to 150-111 ºC with Ce compounds being most effective and non-toxic[52]. Cu and Mn cause filter plugging and toxicity, respectively. These additives reduce smoke opacity, without significantly affecting the overall PM emission[53-56]. Organo-soluble cerium based additives allow 20-40 % PM reduction and lowering of ignition temperature of the accumulated particulates in diesel fuelled bus engines[53]. Cerium remains present in fuel as a hydrocarbon miscible organo-metallic compound which, during combustion, is oxidized leaving CeO_2 as by product. CeO_2 has low acute toxicity, very low solubility in water and acids and is highly inert. Its low level exposure does not pose a risk to human health[57-63]. Further, in a comparatively recent study on catalytic activity of nano-structured cerium oxide films using XRD, XRR and temperature programmed reaction[64], it has been established that smaller grain size of cerium oxide may reduce the activation temperature of carbon combustion as low as about 200 ºC. This property can be explored for soot reduction.

A Ce based organometallic compound has been used by Lemaire[65] as fuel additive in conjunction with cellular ceramic filter as diesel particulate trap oxidizer for diesel particulate emission control in urban buses and reported that 100 ppm of additive concentration caused 100 ºC decrease in trap regeneration temperature without affecting the trap filtration efficiency and base line emissions of engine (mainly NOx), but capturing 90 % of Ce emissions as CeO_2. In presence of trap and 100 ppm concentration of Ce additive, the PM reduction was 83.9 and 78.15 % for DDC 6V 92TA engine equipped with the Donaldson system and RABA/MAN D2156 HM6U engine equipped with PATTAS system, respectively.

Cerium(III) naphthenate with about 6 % cerium concentration has been used as fuel additive in Athens bus fleet requiring servicing every 31000 miles when 10 ppm Ce was used at consumption rate 10 miles/gallon fuel[66]. EOLYS™ system having 30 % cerium is more acceptable in this regard[67]. On combining the catalytic Pt-impregnated soot filter system with an SCR Frauenthal catalyst at GHSV of 520001/(1 h) and Pt/Ce additive mixed diesel fuel, the soot and NOx removal were 98-99 and 40-73 %, respectively[68].

Saitoh[69] reported that the light oil fuel additives containing naphthenates and stearates of Ca, Ba, Fe and Ni are highly effective for soot reduction in diesel engine exhausts. Sulphates and carbonates of Ba were found to reduce smoke level by 50-70 %. An emulsion comprising of oil soluble carboxylic acid salts of V, Cu, Ca and Ba and water soluble compounds $NaHCO_3$ and $KHCO_3$, was found to cause no effect on PM. Alcohol or kerosene solutions of potassium benzoate, calcium salt of 2-ethylhexanoic acid, potassium phthalimide and calcium stearate revealed 30-40 % NOx reduction although

PM reduction was not affected by these additives. Less than 25 % of the barium emitted by diesel engines is in the form of water soluble barium compounds that are usually toxic[70]. In recent reports Ma *et al.*[71] reported the 35-40.7 % soot reduction by 1-4 % concentration of eight organometallic compounds of Ba, Fe (including ferrocene), Cu, Mn and Ce in diesel engine. Guru *et al.*[72] prepared organometallic compounds from oxides of Ca, Mg, Mn and Cu and found them effective for decreasing the freezing point, viscosity and flash point of diesel. Miyamoto *et al.*[73] reported the effect of many soluble diesel fuel additives based on Ba and Ca and found that metal content (and not the metal compound content) was important besides other factors like gas turbulence and excess air factor in soot reduction.

0.2 % Magnesium perchlorate has been reported to reduce diesel smoke emission of vortex type engines by 28 % average[74]. Bimetallic catalysts like KCu and KCo have been reported to cause reduction of NOx and soot by their mutual reaction in diesel engine exhausts[75]. A commercial diesel fuel additive Envirox™ containing nano particles of cerium oxide, has recently been claimed to increase the fuel efficiency and reduce soot[76]. Anti smoke additives produced by the reaction of Fe(III), Mn(III) and Ce(IV) with *tert*-butylperoxide derivatives during pre-ignition fuel combustion, were found to control the soot and PAH specially when combined with a ceramic trap[77]. Recently, a cerium based additive (DPX-9 from Rhodia) has been used for catalytic oxidation of diesel soot in temperature programmed experiments on surface oxygenated complexes and kinetic modelling[44].

Non-metallic additives: European Union and United States have shown their interest in promoting the use of bioenergy[78]. This has led to an increased interest in using oxygenates as additives in diesel fuel. Many reports, related to the reduction of PM on addition of oxygen containing compounds to diesel fuel, are already a part of literature[52-96]. In presence of oxygenates, aldehyde emission increases and NOx emission decreases[52-82]. Alcohols, ethers and esters have been explored in this respect[79,83-88]. PM reduction depends on the percentage of oxygen in compounds and not on chemical nature[89-92]. In one of such studies[89], additive was blended with fuel so as to keep O_2 content at 15 % in a Cummins B 5.9 direct injection diesel engine, the PM reduction was highest in presence of highest oxygen content without being influenced significantly by the chemical structure of the additive. In another study involving a four valve, three cylinder, 1.26 L, prototype diesel engine coupled with common rail fuel injection[90], the highest PM reduction has been reported for di-isobutyl adipate and tripropy-leneglycol monomethyl ether followed by dipropyleneglycol monomethyl ether. Aromatic oxygenate, dibutylphthalate was found to enhance the PM emission. A study on seven oxygenates added to low sulfur fuel and Fischer-Tropsch fuel[91], revealed that the number fraction remained same while volume fraction

increased for the emitted particles. This effect was related to the oxygen content and the oxygen containing functional groups of additive. 15-50 % Blending of butylal-an acetal and oxygenate compound with properties similar to diesel, efficiently reduces the particle size, particle numbers and opacity in the exhaust gas, without affecting the NOx emission[83,95]. An acetal (1,1-diethoxyethane, that can be made from bio based ethanol) when employed as oxygenate additive to diesel fuel in heavy duty diesel engine (Scania 9L compression-ignition diesel engine with electronically controlled fuel injection, used without emission control) has been found to decrease particle number by 23 %, particulate mass by 34.6 % and NOx by 3.2 % without affecting other emissions significantly except the acetaldehyde emission that got quadrupled due to decomposition and oxidation of acetal to acetaldehyde[78].

Sathiyagnanam and Saravanan[97], have recently reported that, 1-5 % (v/v) of the diesel fuel additives dimethoxymethane and dimethoxypropane, can cause reduction in smoke density and PM in the Kirloskar TV-I diesel engine emissions. These reductions were maximum when 3 % of former and 5 % of later additive was used in combination with diesel particulate trap. These fuel additives increase the combustion temperature which, in turn, increases the NOx level. Suzuki *et al.*[98] have experimented non metallic additives of category nitro- and oxygenates (N,N-dimethylacetamide, 2-butanone oxime, isopentilnitrate, 2-ethylhexyl nitrate and *n*-hexylnitrate), oxygenates (dimethylcarbonate, diethyl glycol dimethyl ether, paraldehyde, ethylene glycol mono *n*-butyl ether, polyethylene glycol monooleic acid ester and polyethyleneglycol dioleic acid ester) and nitrogenates (diisopropylamine, diisobutylamine, isopentylamine, dodecylamine, 2,2'-azo*bis*(2,4-dimethylvaleronitrile), piperidine and pyrrolidine). They found that nitrites and nitrates can reduce smoke and PM in the direct fuel injection engine at 2100 rpm and 80 % load. N-hexylnitrite added to gas oil, improved PM/NOx and fuel consumption efficiency in the indirect fuel injection engine under Japanese 10.15 mode operation. They also reported the effect of these additives on cycle to cycle variation of maximum pressure in the cylinder and its stabilization. In a co-operative fuel research engine[99], the addition of commercial ignition improver based on ethyl hexyl nitrate to a base fuel with cetane number 40.2, decreased the NOx and unburned hydrocarbons while the smoke emission was found to increase due to decrease in proportion of injected fuel burnt in relatively small premixed phase. Shi *et al.*[100] used 20 % (v/v) mixture of ethanol and methyl soyate (A) and methyl soyate alone (B) and blended them with diesel to maintain concentration 15 % of A, 20 % of A and 20 % of B. The effect was that PM and NOx emissions decreased and increased, respectively, the effect being maximum in case of 20 % of Serdari *et al.*[101], found that a combination of 200

ppm of H1 and 500 ppm of H2-two commercially available additives (H1 being iso octyl nitrate and H2 being a combustion improver) causes reduction of both PM and NOx in single cylinder stationary diesel engine emissions.

Mixed Diesel-Fuels and additives: A mixed diesel fuel additive containing catane number improver, surfactant, organometallic compounds and xylene was found[102] to suppress soot by 19 %. Three metallorganic additives, fifteen different soot filters and eleven catalytic coatings were examined for their influence on PAH and soot reduction in diesel emissions[103]. Some reports on testing some of the barium based commercial additives for use in underground mines diesel engines, have come up during last few years. However, the possible potential adverse side effects have not been explored[104,105]. The use of blend of diesel fuel with ethanol has been found effective in reduction of PM emissions over two-thirds of the engine map[106]. Blends of diesel fuel containing 0.05 to 0.2 % (w/w) sulphur and 10 % (v/v) biodiesel derived from sunflower oil were subjected to combustion in three conventional diesel engine vehicles and one stationary Petter diesel engine. It was found that combination of low sulphur diesel fuel and biodiesel resulted in reducing the PM emissions at higher loads[107]. Some of the fuel additives out of EHN, DTBP, MTBE, diglyme and ethanol, when added to diesel fuel in Yamaha ME200F 3-cylinder DI engine, had positive effect on exhaust emissions that could be strengthened by increasing the engine operation time[108]. One oxygenated and seven non-oxygenated non-metallic organic compounds showed promising smoke reduction from diesel engine emissions, although further studies were required[109]. In another study, 5-15 % concentration of dimethylcarbonate in diesel fuel was used to observe appreciable reduction of PM emission from multi-cylinder engine[110]. Systematic addition of alcohol to fuel and incorporation of a catalyst on the surface of cooperative fuel research diesel combustion chamber, caused 40-80 % soot reduction[111]. Using a rapid compression machine and an optical engine, significant reduction in soot and NOx has been observed in presence of a mixed fuel consisting of CO_2 as a low boiling point additive and *n*-tridecane representing gas oil of higher boiling point[112]. Studies on single cylinder DI diesel engine using seven types of fuels, revealed that the additive calcium naphthenate was more effective with fuels having higher cetane number and lower kinematic viscosity[113]. The PM reduction effect of (a) 6 % water in diesel emulsion fuel used in Euro-3 light duty diesel vehicle, (b) 12 % of same type of fuel in Euro-2 heavy duty engine and (c) with a cerium based combustion improver additive (AMF-ALFA additive, having two components that are to be mixed and added to fuel; 85 % component-1, which contains a cetane improver, cold properties enhancer and detergent and 15 % component-2 having mixture of organometallic compounds based mainly on Ce), have been reported by Farfaletti *et al.*[114]. The PM reduction was 32 % (mass/km) and 59 % (mass/kWh)

for (a) and (b) respectively. For case (c), PM reduction was 13 % for light duty vehicles. There was no effect on NOx in all cases. Seventeen additives including the commercial compounds to reduce emissions in internal combustion engines, diesel cetane improvers and proprietary additives, injected into JP-8 fuel feed, were assessed and found to be relatively ineffective in reducing the particulate emissions from T 63 helicopters[115].

ADDITIVES FOR OTHER FUELS

Mixtures of ERBS fuel and 7.5-15 % methanol were assessed using prototype multi-fuel injector in a tubular laboratory burner with turbulent swirl stabilized diffusion flame. It caused 37-50 % soot reduction[116]. Methanol, ethanol and MTBE have been found to reduce aromatics, PAH species and soot formation[117]. Mckeand *et al.*[118], used 10 % (v/v) concentration of commercially available additive having cyclohexanone and a mixture of nitroalkanes additives in JP-8 fuel in high pressure model gas turbine combustor and observed 80 % reduction in volume fraction of soot. The same has been proposed by them for trial in ethylene-air flame as the additive may supply NO to flame where NO can reduce soot formation. Substitution of mineral diesel with biodiesels (fatty acid methyl esters)[101] obtained from sunflower oil, corn oil, olive oil and used frying oils, in a single cylinder stationary engine, has been reported to improve the PM emissions and further improvement could be observed in presence of blends of two commercially available additives-H1 (iso octyl nitrate) and H2 (a combustion improver). A review[119], on the effect of biodiesel fuels on diesel engine emissions has come up recently with particular emphasis on the most concerning emissions: NOx and PM, the latter not only in mass and composition but also in size distributions. In this case the highest consensus was found in the sharp reduction in particulate emissions. The effect of dimethyl ether and ethanol on fuel rich premixed ethane combustion was studied by Song *et al.*[120] in a modelling study for a constant pressure reactor model. Dimethyl ether was found to be more effective in reduction of aromatic species that are considered as precursors for soot formation. It may be due to higher enthalpy of formation of dimethyl ether that led to higher final temperature. Modelling study of the effect of dimethyl ether, ethanol and CS_2 added to ethane fuel revealed that the PAH and soot formation is expected to be reduced by using these additives[121].

In a study[122] on the addition of iron pentacarbonyl to cocentric diffusion burner flame of acetylene-ethylene-air, it was found that soot particle size for Fe doped flame was relatively smaller than that of non-doped flame. This particle generating burner system could be used for bioassay for PM_{10} *i.e.* particulate matter with aerodynamic diameter less than 10 μm. In methane co-flow diffusion flames, N_2 is more effective than CO for soot suppression[123]. In a study on the effect of gaseous additives like N_2, Ar, He, H_2 and

CO on C_2H_4, C_3H_8 and C_4H_{10} fuels, Du *et al.*[124] concluded that H_2 with its large diffusivity, is effective at suppressing soot inception in strained flames while addition of CO to alkanes yields a little enhancement in soot chemistry. Ferrocene and iron pentacarbonyl are the most explored additives used in hydrocarbon flames. Reports are available on ferrocene and/ or iron pentacarbonyl seeded laminar premixed ethylene flames[125,126], premixed propane flame[127-129], isooctane diffusion flames operating above its smoke point[130], ethylene diffusion flame[131], ethylene-air non-premixed flame[132], methane/ argon flames[61], acetylene/argon flames[61] and isooctane diffusion flames[1]. *Ex situ* analysis showed that Fe, FeO and Fe_2O_3 are formed and the soot suppression effect is limited to soot burn out zone of flame which is absent in premixed flames generally used in laboratory burners[125-129]. In actual combustors (in which diffusion flames play a key role), this stage is available as the final soot burn out or oxidation state in which soot particles are significantly destroyed *via* OH and oxygen oxidation forming CO or CO_2. Some of the findings[1,61,131,133] are that additives change into iron oxides which are initially reduced (due to reaction with carbon) to elemental iron within the soot particles. This Fe catalyzes the carbon deposition in initial stage which increases the soot particle size and number density. At later residence time, in soot burn out region, these properties are decreased as Fe might get oxidized to form oxides again with the net result that carbon is oxidized. Reports are also available that predict the presence of Fe, FeO, FeO_2, FeOH and $Fe(OH)_2$, in flame[134,135]. Presence of FeO^+, Fe_2O^+ and $Fe_2O_3^+$ has also been indicated on the basis of mass spectrometry of soot particles[136].

In a significant recent report based on *in situ* analysis of laboratory isooctane diffusion flames seeded with 4000 ppm iron pentacarbonyl, by using laser induced fluorescence, thermophoretic sampling and TEM, Kim *et al.*[1] observed 66 % PM reduction. They also found minor soot enhancing effect at early residence time and soot reduction in soot burnout regime. Loss of elemental iron to iron oxide was observed by them on increasing flame residence, suggesting the catalysis of soot oxidation by iron oxide species.

The species dominant at various flame temperatures are $Fe(OH)_2$ and FeO (at 1800 K)[134,135,137], FeO and Fe_3O_4 (at 1000-1200 K, corresponding to flame oxidation region)[1] and Fe_2O_3 (at even lower temperatures)[1].

MODE OF ACTION OF ADDITIVES

Oxygenated additives and biodiesels: Such additives and fuels have molecules that enable more complete combustion even in the regions of combustion chamber with fuel-rich diffusion flames and promote the oxidation of the already formed soot[119,138]. Oxygen content of fuel has already been linked to the PM reduction[139]. An increase of 1 % in oxygen content causes 6-7 % PM reduction[140]. Lower stoichiometric need of air in this

case decreases the probability of fuel rich regions in non-uniform fuel-air mixture, decreasing thereby, the chances of soot formation[141]. The combustion advance responsible for enlargement of the residence time of soot particles in high temperature atmosphere, promotes further oxidation in presence of oxygen[139,142]. In addition to this, there are four more factors responsible for PM reduction in case of biodiesel fuels. These are (a) absence of soot precursors like aromatics[139, 141, 143], (b) different structure of soot particles while using biodiesels[144,145], (c) usually lower boiling point of biodiesel (despite high distillation temperature) due to which the heavy hydrocarbon fractions remain unable to vapourize and change into soot or tar[119] and (d) nil sulphur content in most of the biodiesel fuels that prevents the sulphate formation and the absence of scrubbing effect by which sulphur becomes an active center of hydrocarbon adsorption on the surface of soot particles[146]. It is supported by the observation that 100 ppm decrease in sulphur content causes 3-5 % PM reduction[140].

Nitro-oxygenated additives: The findings that nitrites and nitrates can reduce smoke and PM in the direct fuel injection engine[98] and that in methane co-flow diffusion flames, N_2 is more effective than CO for soot suppression[123], are suggestive that the nitro-oxygenated additives may supply NO to flame where NO can reduce soot formation[118]. The involved reaction may be[147]:

$$2NO + C \rightarrow CO_2 + N_2$$

Organometallic and metallic additives: Organometallic compounds are generally used as additives so as to increase the solubility of the metal in a petroleum fuel. Some of the studies showed no effect of organic ligand[17]. The metal content and not the metal compound content has been found to be important in case of many diesel-soluble fuel additives based on Ba and Ca[73].

Howard and Kausch[17], reviewed the mechanisms of the action of metal additives in bringing down PM and soot. The position described by them is summarized as follows. Na, K, Cs and Ba in particular and all metals to some extent, form ions in flame that act on the molecular and particulate flame ions to decrease the nucleation or coagulation rate. The overall ion concentration increases but the natural flame ion concentration decreases in this process. Charge transfer reactions are also part of the process.

$$M + H_3O^+ \rightarrow M^+ + H^\bullet + H_2O$$
$$Ba + OH^\bullet \rightarrow BaOH^+ + e^-$$
$$BaO + H^\bullet \rightarrow BaOH^+ + e^-$$

Ba, Ca and Sr additives can also act by reaction with flame gases to produce hydroxyl radicals which, in turn, can remove soot or soot precursors like gaseous hydrocarbons. The reactions like

$$H_2O + H^{\cdot} \rightleftharpoons OH^{\bullet} + H_2,$$

are balanced by following reactions

$$M + OH^{\bullet} \rightarrow MOH^{+} + e^{-}$$
$$MO + H^{\bullet} \rightarrow MOH^{+} + e^{-}$$
$$MO + H^{\bullet} \rightarrow M + OH^{\bullet}$$

so that the $OH^{\bullet}$ concentration remains sufficient for accelerating the rate of carbon oxidation,

$$C + OH^{\bullet} \rightarrow CO + H^{\bullet}$$
$$CO + OH^{\bullet} \rightarrow CO_2 + H^{\bullet}$$

Mn, Fe, Co and Ni additives can also act in oxygen rich secondary flame zones by the occlusion of metal in the soot particles and accelerating its oxidation rate. Particularly MMT and ferrocene have been reported to act by this mechanism[17].

Some of the recent reports make the action of ferrocene more clear. Ferrocene reduces the ignition temperature of soot by about 125 ºC and thus helps in PM reduction[148]. Ba acts by different mechanism than Mn or Fe(III) as only it shows significant PM reduction in primary zone flame radiation[149,150]. Fe acts by getting occluded in soot particles, accelerating thereby the rate of oxidation in O_2 rich flame zones[43]. Also the metal oxides are formed which remove carbon of the soot by changing it into CO, general reaction suggested for Mn, Fe, Co and Ni[43] is,

$$M_xO_y + C \rightarrow CO + M_xO_{y-1}$$

Mitchell *et al.*[151-153], investigated the role of ferrocene, ferrocene derivatives and other organometallic compounds of Fe, Zn and Ti in PM inhibition for pool flames and found that 4 % of ferrocene was very effective in enhancing the oxidation rate of soot without affecting, at the same time, the electric charge caused by the loss of electrons *via* thermionic emission. This charge affects the agglomeration within the flame and therefore the size of soot particles[152-154]. Out of various compounds investigated by them, ferrocene and butylferrocene were found to be most effective causing soot reduction up to 96 % in presence of their concentration of 3 % of oil (by weight)[151]. The reactions suggested for the action of ferrocene[151] are,

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2;\ FeO + C \rightarrow Fe + CO$$

Ce changes to cerium oxides in flame. Cerium oxides have a catalytic effect in oxidation of soot. Logothetidis *et al.*[64] explored the catalytic efficiency of CeO_2 and found that smaller grain size of cerium oxide may reduce the activation temperature of carbon combustion as low as about 200 ºC. Vonarb *et al.*[44], in fuels Ce can form $Ce_xO_yS_z$ type particles which decompose and oxidize the SOCs (surface oxygenated complexes which are formed

due to absorption of O_2 on surface defect sites of soot). The decomposition of $Ce_xO_yS_z$ (and not the oxidation of soot) is rate determining step for CO_2 formation. $Ce_xO_yS_z$ are oxygen reservoirs for oxidation of SOCs.

In another study[42], keeping in view that $(Fe(OH)_3$ changes into Fe_2O_3 nano-particles in combustion furnace[32], $Fe(OH)_3$ nonofluid dispersed in diesel and used as additive for PM reduction in the heavy fuel oil-fired combustion boilers under constant condition of 4 % O_2 in flue gas, the following reactions have been proposed:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2;\ Fe_2O_3 + C \rightarrow 2FeO + CO;\ FeO + C \rightarrow Fe + CO$$
$$2FeO + O^* \rightarrow Fe_2O_3;\ 3CO + Fe_2O_3 \rightarrow 3CO_2 + 2Fe$$

The observed non-significant effect of this additive on NOx reduction, under constant suppply of O_2, was explained on the basis of following reactions[42]:

$$3CO + Fe_2O_3 \rightarrow 3CO_2 + 2Fe;\ 2FeO + O^* \rightarrow Fe_2O_3$$
$$2Fe + 3NO \rightarrow 1.5N_2 + Fe_2O_3;\ Fe_2O_3 + C \rightarrow 2FeO + CO$$
$$2FeO + NO \rightarrow Fe_2O_3 + 0.5N_2$$

On the basis of combination of laser induced fluorescence experimental observations (already described earlier) and equilibrium calculations that indicated the importance of Fe_3O_4 and Fe_2O_3 formation for soot reduction with increase in flame residence time, Kim *et al.*[1], considered it more reasonable to assume oxidation of elemental iron and subsequent catalysis by iron oxide species, in addition to the catalysis by elemental iron. Thus main reactions going on in flame should be as follows[1,61,131,133-136].

$$C + FeO \rightarrow CO + Fe;\ C + O_2 + Fe \rightarrow CO_2 + Fe$$
$$C + OH + Fe \rightarrow CO + H + Fe;\ 2Fe^* + O_2 \rightarrow O^* + O^*$$
$$Fe^* + H \rightarrow H^*;\ O^* + H^* \rightarrow OH;\ Fe + O_2 \rightarrow FeO \text{ or } Fe_2O_3 \text{ or } Fe_3O_4$$
$$C + O_2 + FeO \text{ or } Fe_2O_3 \text{ or } Fe_3O_4 \rightarrow CO_2 + FeO \text{ or } Fe_2O_3 \text{ or } Fe_3O_4$$

It is clear from the literature reviewed above that the problem of simultaneous PM and NOx reduction needs to be addressed more vigorously. Still, there is need to avoid the trade-off between PM and NOx emissions and it seems that the same requires complex methodology. If both, NOx and PM reduction, are not achievable simultaneously, it would be better to reduce one emission at the cost of other that can be removed by after treatment[3]. One of the possibilities seems to be the application of metal nano-fluids for this purpose and further work is required in this direction.

ACKNOWLEDGEMENTS

The authors are thankful to Ministry of Environment, Republic of Korea for financial assistance and one of the authors Dr. R.D. Kaushik is also thankful to KOFST (Korean Federation of Science and Technology Societies) for invitation as Brain Pool Scientist for undertaking this research work.

REFERENCES

1. K.B. Kim, K.A. Masiello and D.W. Hahn, *Combust. Flame*, **154**, 164 (2008).
2. E.J. Highwood and R.P. Kinnersley, *Environ. Int.*, **32**, 560 (2006).
3. J.P.A. Neeft, M. Makkee and J.A. Moulijin, *Fuel Process. Technol.*, **47**, 1 (1996).
4. G. Obberdorster, *Int. Arch. Occup. Environ. Health*, **74**, 1 (2001).
5. M.F. Denissenko, A. Pao, M.S. Tang and G.P. Pfeifer, *Science*, **274**, 430 (1996).
6. K. Ravindra, R. Sokhi and R.V. Grieken, *Atmosph. Environ.*, **42**, 2895 (2008).
7. W.C. Malm and D.E. Day, *Atmosph. Environ.*, **34**, 3373 (2000).
8. National Academy of Sciences, Particulate Polycyclic Organic Matter, Washington DC, p. 30 (1972).
9. H.S. Stoker, S.L. Seager and R.L. Capener, Energy, Scott Foresman, Glenview, Illinois, p. 163 (1975).
10. A. Dipple, Chemical Carcinogens, Am. Chem. Soc. Monograph 173, Washington D.C., p. 245 (1976).
11. T. Johnson, *Platinum Met. Rev.*, **52**, 23 (2008).
12. K. Przybilla, H. Burtscher, Z. Quian and U. Matter, *Combust. Sci. Technol.*, **174**, 49 (2002).
13. A. Rebola and M. Costa, *Proc. Combust. Inst.*, **29**, 2243 (2002).
14. F.T. Kelly, J.P. Liddy, H. Sutherland, G.W. Sutton and D.M. Whitehead, *Erdol Kohle. Erdgas. Petrochem.*, **42**, 408 (1989).
15. L. Witzel, P. Moszkowicz and G. Claus, *Fuel*, **74**, 1881 (1995).
16. M. Ferrara, Proceedings of 5th International Conference on Technologies and Combustion for a Clean Environment, Lisbon, p. 425 (July 1999).
17. J.B. Howard and W.J. Kausch, *Prog. Energy Combust. Sci.*, **6**, 263 (1980).
18. DIN 51 402 Teil 1, Berlin (1986).
19. Luftrienhalte-Verordnung vom 16, Swiss Federal Law, SR 814.318.142.1 (1985).
20. B.S. Haynes and H.G. Wagner, *Prog. Energy Combust. Sci.*, **7**, 229 (1981).
21. A. Poullikkas, *The Cyprus J. Sci. Technol.*, **3/2**, 81 (2001).
22. J. Davies, J.W. Lexton and M.J. Owers, *J. Inst. Energy*, **14**, 21 (1981).
23. G.B. Martin, D.W. Pershing and E.E. Berkau, U.S. EPA, Office of Air programs, RTP, Pub. No. AP-87 (1971).
24. D.B. Giovanni, P.G. Pagni, R.F. Sawyer and L. Hughes, *Combust. Sci. Tech.*, **6**, 107 (1972).
25. P.G. Pagni, L. Hughes and T. Novakov, NATO/AGARD meeting paper no. 25, London, NTIS no. AD769278 (1973).
26. S. Hersh, J.S. Hurley and R.C. Carr, Presented at Meeting of Air Pollution Control Association, Portland, Oregon (1976).
27. A.F. Klarman, Evaluation of Smoke Suppressant Fuel Additives for Jet Engine Test Cell Smoke Abatement, NAPTC-PE-103 (1977).
28. R.J. Sullivan, Air Pollution Aspects of Manganese and Its Compounds, National Air Pollution Control Administration, NTIS, PB 188 079 (1969).
29. D.C. Kim, J.H. Kim, J.K. Woo, N.S. Nho, D.H. Shin and R.D. Kaushik, *Asian J. Chem.*, **20**, 5760 (2008).
30. R.J. Sullivan, Air Pollution Aspects of Iron and Its Compounds, National Air Pollution Control Administration, NTIS, PB 188 088 (1969).
31. R.L. Weeks, W.L. Clinkenbeard and J.D. Solties, Proc. Fifth World Petroleum Congress, section VI, p. 381 (1959).
32. A. Cotton, G. Wilkinson, C.A. Murillo and M. Bochmann, Advanced Inorganic Chemistry, 6th edition, John Wiley & Sons, N. York (1999).
33. R.J. Hartle and J.R. McGuire, US Patent, 3,082,071 (1963).
34. A.V. Churchill and E. Mitchell, US Patent, 2,971,828 (1961).

35. J.J. Vaerman, *J. Inst. Petrol.*, **50**, 155 (1964).
36. D.W. Pershing, G.B. Martin, E.E. Berkau and R.E. Hall, U.S. EPA Report no. EPA-650/2-73-031 (1973).
37. J.S. Lighty, J.M. Veranth and A.F. Serofim, *J. Air Waste Manag.*, **50**, 1565 (2000).
38. J.C. Brien, *J. Inst. Energy*, **15**, 115 (1982).
39. P. Davini and R. Tartarelli, *Fuel*, **64**, 380 (1985).
40. A. Poullikkas, *Energy Convers. Manag.*, **45**, 1725 (2004).
41. J.H. Kim, J.K. Woo, N.S. Nho, D.C. Kim, R.D. Kaushik, Y.C. Jang and Y.S. Lee, Proceedings of 46th Conference of Korean Society for Atmospheric Environment, Seoul, PE-1, 601-603 (2008).
42. D.C. Kim, J.H. Kim, J.K. Woo, D.H. Shin, Y.S. Lee and R.D. Kaushik, *Asian J. Chem.*, **20**, 5767 (2008).
43. D.H. Cotton, N.J. Friswell and D.R. Jenkins, *Combust. Flame*, **17**, 87 (1971).
44. R. Vonarb, A. Hachimi, E. Jean and D. Bianchi, *Energy Fuels*, **19**, 35 (2004).
45. U. Matter and K. Siegmann, *J. Aerosol Sci.*, **28(S)**, 51 (1997).
46. M. Kasper, K. Sattler, K. Siegmann, U. Matter and H.C. Siegmann, *J. Aerosol Sci.*, **30**, 217 (1999).
47. H. Burtscher, U. Matter and G. Skillas, *J. Aerosol Sci.*, **30(S)**, 851 (1999).
48. H. Burtscher and U. Matter, Society of Automotive Engineers (SAE), Paper no. 2000-01-1883, 1334 (2000).
49. H. Burtscher and H.C. Siegmann, *Combust. Sci. Technol.*, **101**, 327 (1994).
50. C. Huglin, L. Scherrer and H. Burtscher, *J. Aerosol Sci.*, **28**, 1049 (1997).
51. D. Steiner and H. Burtscher, *Environ. Sci. Technol.*, **28**, 1254 (1994).
52. General Motors, US Patent, 4,568,357 ( ).
53. B. Martin and D. Harrier, Proceed. Seminar British Institute of Mechanical Engineers, London, Fuels for Automotive and Industrial Engines, p. 77 (1990).
54. B. Weidmann and K. Neumann, SAE paper 850017 (1985).
55. G.M. Simon and T.L. Stark, SAE Paper 850016 (1985).
56. V.D. Rao, J.E. White, W.R. Wade, M.G. Aimone and H.A. Cikanek, SAE paper 850014 (1985).
57. P. Arvela, Toxicity of Rare Earths in Progress in Pharmacology, Gustav Fischer, New York, Vol. 2(3), pp. 69-114 (1979).
58. J.P. Guillot, Institut Francais De Toxicologie, Report, no. 302314 (1983).
59. T.J. Haley, *J. Pharmac. Sci.*, **54**, 663 (1965).
60. G. Monnot, Institut Francais De Toxicologie, Report, no. 301229 (1983).
61. J. Nappee, J. Bobrie and D. Lambard, *Arch. Mal. Prof.*, **33**, 13 (1972).
62. R.J. Palmer, J.L. Butenhoff and J.B. Stevens, *Environ. Res.*, **43**, 142 (1987).
63. J. Traynard, Institut Francais De Toxicologie, Report, No. 302217 (1983).
64. S. Logothetidis, P. Patsalas and C. Charitidis, *Mater. Sci. Engg.*, **C23**, 803 (2003).
65. J. Lemaire, Proceedings SAE TopTec Symposium, Atlanta (1993).
66. K. Pattas, Z. Samaras, D. Sherwood and L.S. Socha Jr., SAE Tech. Pap. Ser., Paper no. 940235 (1995).
67. J.C. Summers, S.V. Houtte and D. Psaras, *App. Catal. B: Environ.*, **10**, 139 (1996).
68. M. Makkee, H.C. Krijnsen, S.S. Bertin, H.P.A. Calis, C.M. van den Bleek and J.A. Moulijn, *Catal. Today*, **75**, 459 (2002).
69. Y. Saitoh, *Tsukuba Ind. College Res. Lab. Pub.*, **35**, 113 (2000).
70. R.J. Sullivan, Air Pollution Aspects of Barium and Its Compounds, National Air Pollution Control Administration, NTIS, PB 188 083 (1969).
71. L.C. Ma and Y. Liu, *J. Fuel Chem. Technol.*, **34**, 230 (2006).
72. M. Guru, U. Karakaya, D. Altiparmak and A. Alicilar, *Energy Conver. Manag.*, **43**, 1021 (2002).

73. N. Miyamoto, Z. Hou, A. Harada, H. Ogawa and T. Murayama, *Trans. Japan Soc. Mech. Engineers*, **54**, 484 (1988).
74. T. Kawaraya, K. Funasaka, T. Kamiura, T. Miyazaki and M. Warashina, *World Clean Air Congress*, **5**, 6 (1998).
75. N. Nejar, J.M. Garcia-Cortes, C.S.M. Lecea and M.J.I. Gomez, *Catal. Commun.*, **6**, 263 (2005).
76. G. Wakefield, X. Wu, M. Gardener, B. Park and S. Anderson, *Technol. Anal. Strat. Manag.*, **20**, 127 (2008).
77. R.G. Fazliakhmetov, G.S. Shpiro, I.V. Sal'nikova and E.V. Parfenov, *Khim. Tekhnol. Topliv Masel*, **4**, 42 (1997).
78. K.E Nord and D. Haupt, *Environ. Sci. Technol.*, **39**, 6260 (2005).
79. K.C. Corkwell, M.M. Jackson and D.T. Daly, SAE Tech. Pap. Ser., paper no. 2003-01-3283 (2003).
80. J. Hood and R. Farina, SAE Tech. Pap. Ser., paper no. 952403 (1995).
81. B.Q. He, J.X. Wang, X.G. Yan, X. Tian and H. Chen, SAE Tech. Pap. Ser., paper no. 2003-01-0762 (2003).
82. M. Stoner and T. Litzinger, SAE Tech. Pap. Ser., paper no. 1999-01-1475 (1999).
83. A. Bertola and K. Boulouchos, SAE Tech. Pap. Ser., paper no. 2000-01-2885 (2000).
84. P. Mohanan, N. Kapilan and R.P. Reddy, SAE Tech. Pap. Ser., paper no. 2003-01-0760 (2003).
85. M.D. Kas, J.F. Thomas, J.M. Storey, N. Domingo, J. Wade and G. Kenreck, SAE Tech. Pap. Ser., paper no. 2000-01-2018 (2000).
86. J.C. Ball, M.A. Gonzales, C. Lapin, E. Liney, J. Buckingham, E. Frame, D. Yost, M. Natarajan, J. Garbak and J.P. Wallace, SAE Tech. Pap. Ser., paper no. 2001-01-3627 (2001).
87. J.C. Ball, M.A. Gonzales, C. Lapin, E. Liney, J. Buckingham, E. Frame, D. Yost, M. Natarajan, J. Garbak and J.P. Wallace, SAE Tech. Pap. Ser., paper no. 2001-01-3628 (2001).
88. J.C. Ball, M.A. Gonzales, C. Lapin, E. Liney, J. Buckingham, E. Frame, D. Yost, M. Natarajan, J. Garbak and J.P. Wallace, SAE Tech. Pap. Ser., paper no. 2001-01-3630 (2001).
89. A.S. Chang, R.W. Dibble and B.A. Buchholz, SAE Tech. Pap. Ser., paper no. 2002-01-1705 (2002).
90. D.L. Hildon, J.C. Eckstrom and L.R. Wolf, SAE Tech. Pap. Ser., paper no. 2001-01-0650 (2001).
91. B.E. Hallgren and J.B. Heywood, SAE Tech. Pap. Ser., paper no. 2002-01-0648 (2002).
92. L.I. Yeh, J.L. Rickeard, J.L.C. Duff, J.R. Bateman, R.H. Schlosberg and R.F. Caers, SAE Tech. Pap. Ser., paper no. 2001-01-2019 (2001).
93. M. Natarajan, M.A. Gonzales, E.A. Frame, D.W. Naegeli, E. Liney, T. Asmus, P. Piel, W. Clark, J.P. Wallace and J. Garbak, SAE Tech. Pap. Ser., paper no. 2001-01-3631 (2001).
94. M.A. Gonzales, E. Liney, P. Piel, M. Natarajan, T. Asmus, D.W. Naegeli, D. Yost, E.A. Frame, W. Clark, J.P. Wallace and J. Garbak, SAE Tech. Pap. Ser., paper no. 2001-01-3632 (2001).
95. A. Bertola, R. Schubiger, A. Kasper, U. Matter, A.M. Forss, M. Mohr, K. Boulouchos and T. Lutz, SAE Tech. Pap. Ser., paper no. 2001-01-3573 (2001).
96. N. Miyamoto, H. Ogawa, Arima and K. Miyakawa, SAE Tech. Pap. Ser., paper no. 962115 (1996).
97. A.P. Sathiyagnanam and C.G. Saravanan, *Fuel*, **87**, 2281 (2008).
98. K. Suzuki, K. Yuge, K. Uchikawa and K. Kakugawa, *J. Japan Petrol. Inst.*, **48**, 229 (2005).
99. N. Ladommatos, M. Parsi and A. Knowles, *Fuel*, **75**, 8 (1996).

100. X. Shi, Y. Yu, H. He, S. Shuai, J. Wang and R. Li, *Fuel*, **64**, 1543 (2005).
101. A. Serdari, K. Fragioudakis, S. Kalligeros, S. Stournas and E. Lois, *J. Engg. Gas Turb. Power*, **122**, 624 (2000).
102. L.C. Ma, *Acta Petrolei Sinica*, **23**, 93 (2007).
103. U. Hoffmann, Th. Riekmann and K. Schaduch, *Erdoel Erdgas Kohle*, **110**, 163 (1994).
104. Unites States, Bureau of Mines, Information Circular, p. 79 (1987).
105. Unites States, Bureau of Mines, Information Circular, 9238, p. 17 (1990).
106. R.L. Cole, R.B. Poola, R. Sekar, J.E. Schaus and P. McPartlin, SAE paper no. 2001-01-1937 (2001).
107. A. Serdari, K. Fragioudakis, C. Teas, F. Zannikos, S. Stournas and E. Lois, *J. Propul. Power*, **15**, 224 (1999).
108. L.K.L. Shih, *Am. Soc. Mech. Engineers, ICE Publication*, **33**, 69 (2000).
109. V. Gurumani, S. Senthilvelan, M. Ramajayam and A.R. Ramanathan, *Asian J. Chem.*, **15**, 693 (2003).
110. T. Nibin, A.P. Sathiyagnanam, S. Sivaprakasam and C.G. Saravanan, *J. Inst. Engineers (India). Mech. Engg. Div.*, **86**, 51 (2005).
111. J. Gaffney, R. Sapiemza, T. Butcher, C. Krishna, W. Marlow and T. O'Hare, *Combust. Sci. Technol.*, **24**, 89 (1980).
112. J. Senda, Y. Wada, D. Kwano and H. Fujimoto, *Int. J. Engine Res.*, **9**, 15 (2008).
113. N. Miyamoto, H. Ogawa, Z. Hou and M. Shibuya, *SAE Transactions*, **100**, 276 (1991).
114. A. Farfaletti, C. Astorga, G. Martini, U. Manfredi, A. Mueller, M. Rey, G. De Santi, A. Krasenbrink and B.R. Larsen, *Environ. Sci. Technol.*, **39**, 6792 (2005).
115. E. Corporan, M. DeWitt and M. Wagner, *Fuel Process. Technol.*, **85**, 727 (2004).
116. A.J. Izquierdo and D.P. Hoult, *J. Engg. Gas Turb. Power*, **107**, 734 (1985).
117. F. Inal and S.M. Senkan, *Combust. Sci. Technol.*, **174**, 1 (2000).
118. M. Mckeand, A. Menon, S.Y. Lee, S.R. Saretto and R.J. Santoro, International Symposium on Combustion, Abstracts of Works in Progress Posters, p. 126 (2004).
119. M. Lapuerta, O. Armas and J.R. Fernandez, *Prog. Energy Combust. Sci.*, **34**, 198 (2008).
120. K.H. Song, P. Nag, T.A. Litzinger and D.C. Haworth, *Combust. Flame*, **135**, 341 (2003).
121. J.K. Park, *Int. J. Automotive Technol.*, **7**, 501 (2006).
122. G. Yang, *J. Air Waste Manag. Assoc.*, **54**, 898 (2004).
123. J.R. Arthur and D.H. Napier, Proc. 5th International Symposium on combustion, The combustion Institute, Pittsberg, p. 306 (1955).
124. D.X. Du, R.L. Axelbaum and C.K. Law, *Combust. Flame*, **102**, 11 (1995).
125. K.E. Ritrievi, J.P. Longwell and A.F. Sarofim, *Combust. Flame*, **70**, 17 (1987).
126. A.S. Fietelberg, J.P. Longwell and A.F. Sarofim, *Combust. Flame*, **92**, 241 (1993).
127. D.W. Hahn and T.T. Charalampopoulos, *Proc. Combust. Inst.*, **24**, 1007 (1992).
128. P.A. Bonczyk, *Combust. Sci. Technol.*, **59**, 143 (1988).
129. B.S. Haynes, H. Jander and H.G. Wagner, *Ber. Bunsen-ges. Phys. Chem.*, **84**, 585 (1980).
130. P.A. Bonczyk, *Combust. Flame*, **87**, 233 (1991).
131. J. Zhang and C.M. Megaridis, *Combust. Flame*, **105**, 528 (1996).
132. J. Zhang and C.M. Megaridis, *Combust.Flame*, **105**, 528 (1996).
133. J. Zhang and C.M. Megaridis, *Proc. Combust. Inst.*, **25**, 593 (1994).
134. M.D. Rumminger and G.T. Linteris, *Combust. Flame*, **123**, 82 (2000).
135. M.D. Rumminger and G.T. Linteris, *Combust. Flame*, **128**, 145 (2002).
136. S.H. Kim, R.A. Fletcher and M.R. Zachariah, *Environ. Sci. Technol.*, **39**, 4021 (2005).
137. B. Guo and I.M. Kennedy, *Aerosol Sci. Technol.*, **41**, 944 (2007).
138. C.D. Rakopoulos, D.C. Rakopoulos, D.T. Hountalas, E.G. Giakoumis and E.C. Andritsakis, *Fuel*, **86**, (2007).
139. K. Schmidt and J.H. Van Gerpan, SAE paper no. 961086 (1996).

140. T.L. Ullman, K.B. Spreen and R.L. Mason, SAE paper no. 941020 (1994).
141. M. Lapuerta, O. Armas and R. Ballesteros, SAE paper no. 2002-01-1657 (2002).
142. D.Y. Chang and J.H. Van Gerpan, SAE paper no. 971684 (1997).
143. W.G. Wang, D.W. Lyons, N.N. Clark, M. Gautam and P.M. Norton, *Environ Sci. Technol.*, **34**, 933 (2000).
144. A.L. Boehman, J. Song and M. Alam, *Energy Fuels*, **19**, 1857 (2005).
145. J. Song, M. Alam, A.L. Boehman and U. Kim, *Combust. Flame*, **146**, 589 (2006).
146. A. Duran, J.M. Monteagudo, O. Armas and J.J. Hernandez, *Fuel*, **85**, 923 (2006).
147. S. Kureti, W. Weisweiler and K. Hizbullah, *Appl. Catal. B: Environ.*, **43**, 281 (2003).
148. B.S. Chittawadge and A.N. Voinov, *Indian J. Technol.*, **3**, 209 (1965).
149. N.J. Friswell, in Emissions from Continuous Combustion Systems, Plenum Press, New York, p. 161 (1972).
150. M.W. Shayeson, SAE Paper no. 670866 (1967).
151. J.B.A. Mitchell, *Combust. Flame*, **86**, 179 (1991).
152. J.B.A. Mitchell, D.J.M. Miller and M. Sharpe, *Combust. Sci. Technol.*, **74**, 63 (1991).
153. J.B.A. Mitchell and D.J.M. Miller, *Combust. Flame*, **75**, 45 (1989).
154. P. Bonczyk, *Combust. Flame*, **51**, 219 (1983).

(*Received*: 12 June 2008; *Accepted*: 20 June 2008) AJC-6613