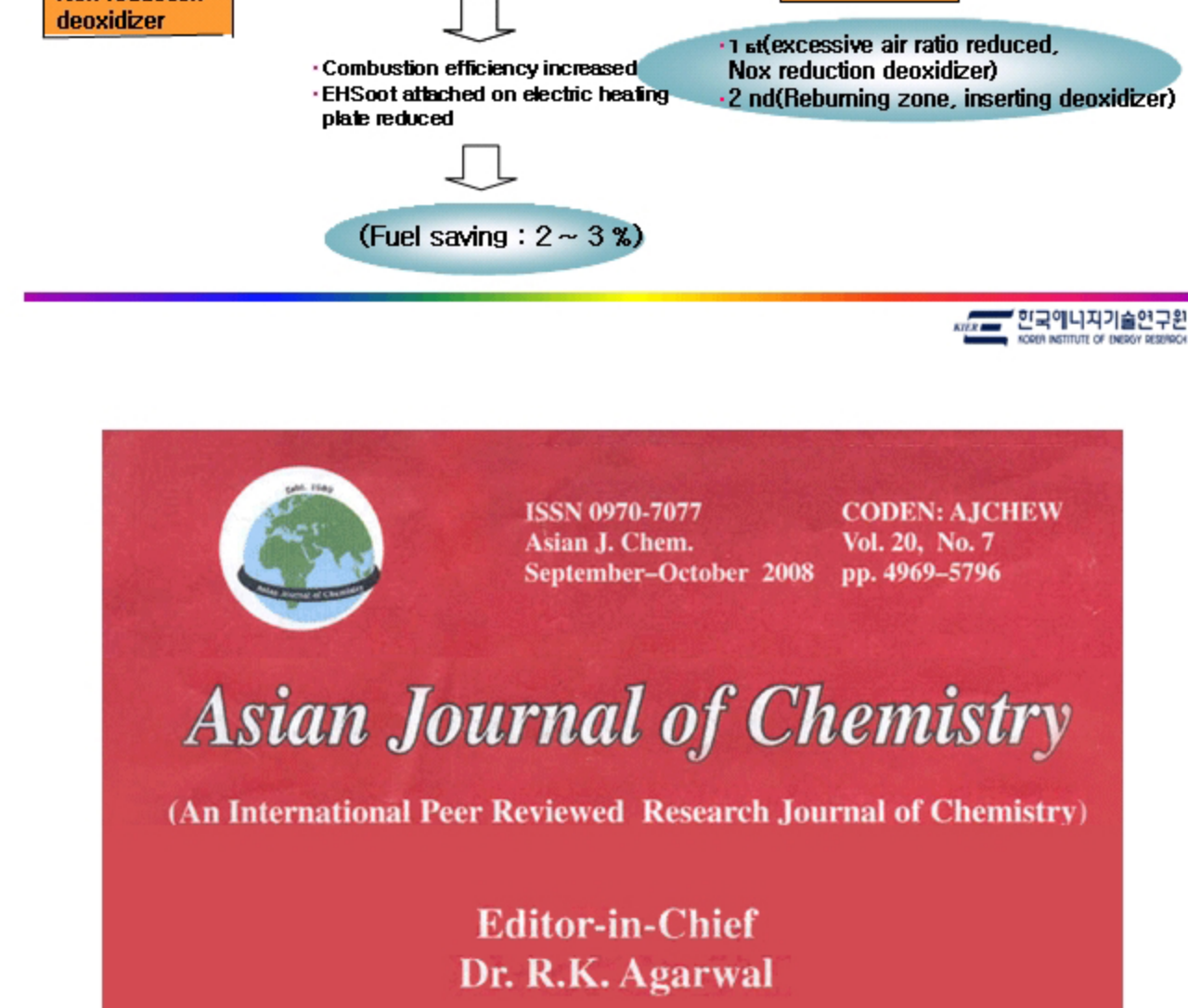


- Research Institute : Korea Institute of Energy Research
- Participating Business : Technobio
- Entrusted Research Institute : Nano Technology Lab., Konyang Univ.

○ R&D Objectives



A New Iron-Nanofluid as Fuel additive for Particulate Matter Reduction in Heavy Fuel Oil – Fired Boiler Facility

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ABSTRACT

Preparation and utilization method of a new Fe-nanofluid based heavy fuel oil additive for PM reduction in heavy fuel oil fired boiler facilities have been presented and discussed. The nanofluid contained average particle size of 22 nm and is cost effective as it was prepared from industrial waste iron sulphate by simple methodology. The additive was found to reduce PM by 53.3% at an active metal concentration of 100 ppm without affecting the NOx content of the gas significantly – a condition that is desirable for avoiding the trade-off between PM and NOx emission which otherwise requires complex methodology. Proper explanations for the effects including the mechanism and reactions involved have also been discussed.

INTRODUCTION

Dust or particulate matter (PM) becomes black smoke when present in sufficient particle size and quantity in exhaust gases resulting from incomplete combustion of hydrocarbon fuels. Generally PM is composed of about 70% carbon and 30% SiO₂, Al₂O₃, etc. In low efficiency furnaces the former is high and later is low while it is reverse case for the high efficiency furnaces. The size of PM particles makes its ingestion deep into the lungs and the polynuclear aromatic hydrocarbon absorbed on PM particles can cause cancer due to

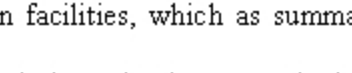
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which stricter emission limits have been proposed [1-4]. The trade-off between PM and NOx emission should be avoided and it requires complex methodology [5]. Therefore, such fuel additives are required that can reduce PM without affecting NOx emission [6]. 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 surfaces sometimes prohibit their use [1]. Manganese usually converts into MnO, Mn₂O₃, MnO₂ or Mn₃O₄ as combustion products in boilers and gas turbines, the amount of these oxides being dependent on the temperature of the process [7-11]. High atmospheric concentration of these oxides results in chronic manganese poisoning, manganese pneumonia and catalytic oxidation of other air pollutants to undesirable products [12]. Less than 25% of the barium emitted by diesel engines is in the form of water soluble barium compounds that are usually toxic [13]. Iron additives and their combustion products are safest of these three metals. The widely used Fe compound Ferrocene has been exploited extensively in animal feeding studies which show almost absence of toxicity although high concentration of iron oxide can cause irritation [14].

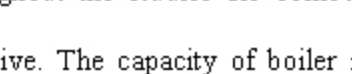
Ferrocene (dicyclopentadienyl iron) has been found to be the most effective PM reduction additive in oil heating combustors in the utility and domestic boilers, in comparison to sulphates of Ni, Co, Mn, Pb and Mg [15]. An iron chelate in large concentrations of 0.01 – 0.08% (w/w) in fuel has been reported to be more effective than 0.05% hydrazine [16-17] or copper sulphate [18]. Transition metal complexes having 20% Fe and 25% Mn were found to be most effective for PM reduction in oil fired domestic boilers [1]. Seven most effective effective additives based on Fe, Mn, Ca and Co were found by Martin et al [19] to cause 53% – 69% PM reduction in residual 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 [1]. MMT (methylcyclopentadienyl manganese tricarbonyl) has been found to be good PM reduction agent in boilers [7], although it increases the PM in cleaner combustors [1] and toxicity of its combustion products (various oxides of Mn) is still controversial [7-9].

Ferrocene reduces the ignition temperature of soot by about 125°C and thus helps in PM reduction [20]. Ba acts by different mechanism than Mn or Fe (III) as only it shows significant PM reduction in primary zone flame radiation [21-22]. Fe acts by getting occluded in soot particles, accelerating thereby the rate of oxidation in O₂ rich flame zones [23]. 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 [23] is,



Mitchell et al 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 by 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 [24-27]. 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) [24]. The reactions suggested for the action of ferrocene [24] are,



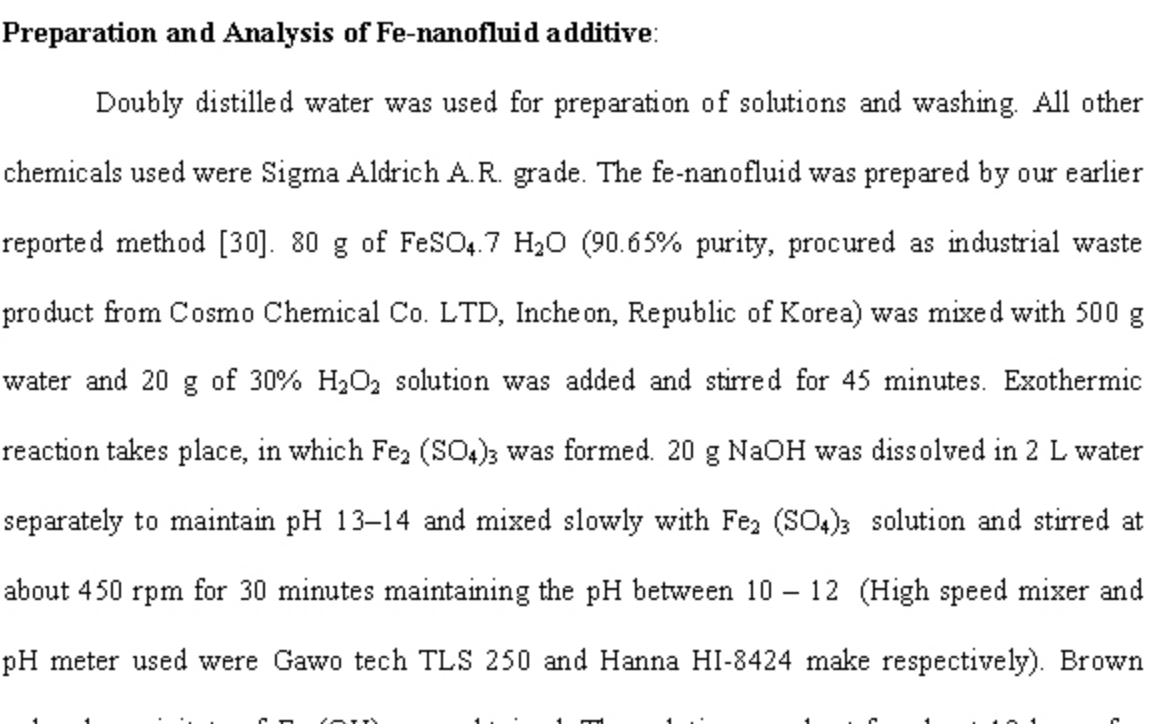
Witzel et al [6] reported the PM reduction by four organometallic additives based on Co, Fe, and Ca for heavy fuel oil combustion and found that 90 ppm Fe concentration caused 29% and 62% PM reduction in presence of two organometallic compounds (exact structure not given) in 1.16 MW boiler. They concluded that metal makes the atmosphere more reactive by promoting the heterogeneous surface reaction and by lowering the ignition temperature, it allows more time for the atmosphere 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 atmosphere and thus, making it more effective. In recent reports Ma et al reported the 35% - 40.7% soot reduction by 1% - 4% concentration of eight organometallic compounds of Ba, Fe (including ferrocene), Cu, Mn, Ce in diesel engine [28]. Oeru et al prepared organometallic compounds from oxides of Cu, Mg, Mn and Ca and found them effective for decreasing the freezing point, viscosity and flash point of diesel [29].

In the present communication, we are reporting the preparation of a new Fe-nanofluid containing Fe(OH)₃ in diesel starting from industrial waste containing FeSO₄·7H₂O and the studies on PM reduction by it in heavy fuel oil-fired combustion boilers. An improved efficiency is expected as in the combustion furnace, Fe(OH)₃ is expected to convert into Fe₂O₃ in combustion facilities, which as summarized above, is effective for PM reduction. Further improvement in its action is expected when it is added in the form of nanofluid as an increase in surface area will facilitate the occlusion of metal in soot particles accelerating thereby the rate of oxidation in O₂ rich flame zones [23]. The additive investigated by us, is simple to prepare, involves less cost of preparation (as the industrial waste sample of iron sulphate involving low cost, was used for preparation of Fe-nanofluid) and operation, and its effect is comparable to many of the other additives already reported.

MATERIALS AND METHODS

Smoke tube type boiler based on combustion of heavy oil was used. The experimental set up for the same is shown in figure -1. The burner, boiler and operational conditions were kept constant throughout the studies for combustion of heavy fuel oil with or without Fe-nanofluid fuel additive. The capacity of boiler in terms of heavy oil combustion and steam generation was 15 L/h and 0.2 T/h respectively. One type oil pressure burner was used. Preheating time was 1 hour. The fuel oil atomizing temperature and atomizing pressure were maintained at 150°C and 22 Kg/cm² respectively. Rate of flow of heavy oil (fuel consumption) was maintained at 10 Kg/h giving a set load factor of 72.54%. The rate of flow of input combustion air and heating were controlled to observe 4% O₂ and temperature 240°C respectively in flue or stack gas.

For collecting the samples of dust from flue gas, the Stack Gas sampling system (model sampling train, 511/213) of Clean Air Express (U.S.A.) was employed. The PM samples were analyzed by weighing after collecting in Tinsolve filter tubes and drying at 200°C for one hour. Thinable filters (HF, 25 mm x 90 mm) were procured from Toyo Koshi Kaisha LTD., Japan.

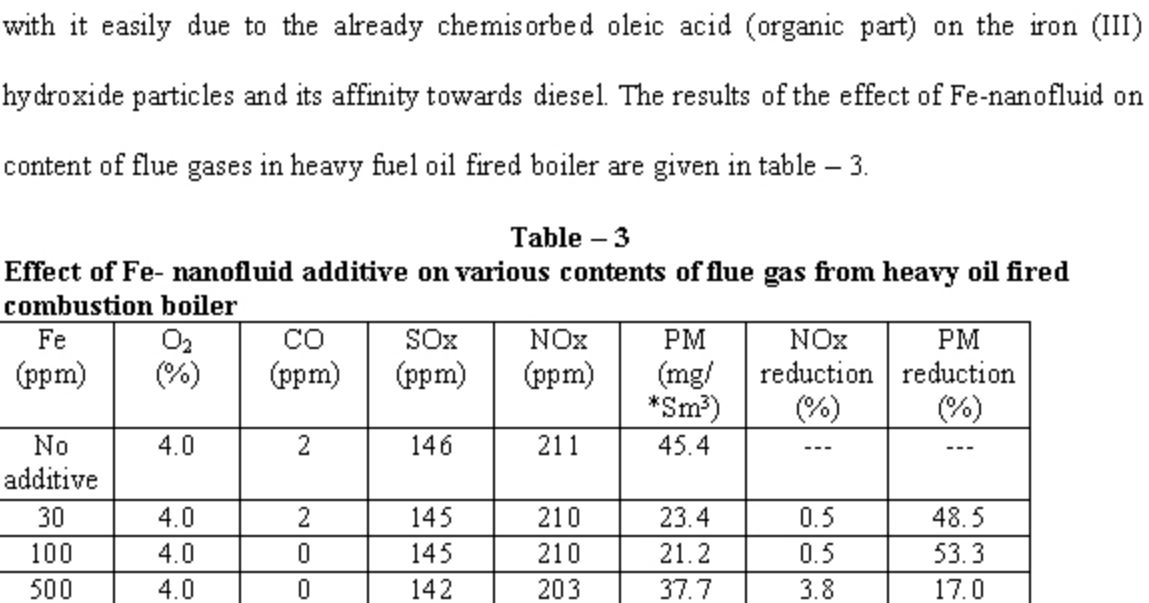


The results of analysis and properties of the commercial heavy fuel oil used for combustion are shown in Table -1 and 2

Content	C	H	N	S	O	Ash	Water*
%, (W/W)	86.7	11.9	0.31	0.27	0.1	0.01	0.05
*%, (V/V)							

Calorific value K cal/kg	Specific gravity @ 4 °C	Viscosity @ 20°C, cSt	Boiling Point °C
10577	0.919	19	231

Preparation and Analysis of Fe-nanofluid additive
 Doubly distilled water was used for preparation of solution and washing. All other chemicals used were Sigma Aldrich A.R. grade. The Fe-nanofluid was prepared by our earlier reported method [30]. 30 g of FeSO₄·7H₂O (98.9% purity, procured as industrial waste product from Cosmos Chemical Co. LTD, Incheon, Republic of Korea) was mixed with 500 g water and 20 g of 30% H₂O₂ solution was added and stirred for 45 minutes. Exothermic reaction takes place, in which Fe₂(SO₄)₃ was formed. 20 g NaOH was dissolved in 2 L water separately to maintain pH 13-14 and mixed slowly with Fe₂(SO₄)₃ solution and stirred at about 450 rpm for 30 minutes maintaining the pH between 10 – 12 (High speed mixer and pH meter used were Geco tech TLE 250 and Hanna HI-8424 mark respectively). Brown colored precipitate of Fe(OH)₃ was obtained. The solution was kept for about 12 hours for allowing the precipitates to settle down. The precipitates was washed with 2 L water. 1 L water was added to precipitates and stirred with 30 ml of oleic acid for 45 minutes at 20-30°C for chemo-reduction of oleic acid molecules on Fe(OH)₃ particles. Now, 1L diesel was added and stirring continued for further 30 minutes. After allowing the sedimentation for 2 – 3 days, lower layer was removed and upper reddish layer was separated and placed for 1 more day for checking the sedimentation, if any. This transparent reddish brown colored nanofluid of Fe(OH)₃ in diesel was stable for over 8 months. The Fe content analysis was performed by ICP-AES technique (Jobin-Yvon Ultima-C model). For particle size analysis, Microtec particle size analyzer model Nanotec NPA210 was used. The analysis revealed that this Fe-nanofluid contained 1.69% Fe and average particle size of 22.48 nm (Fig. 2).

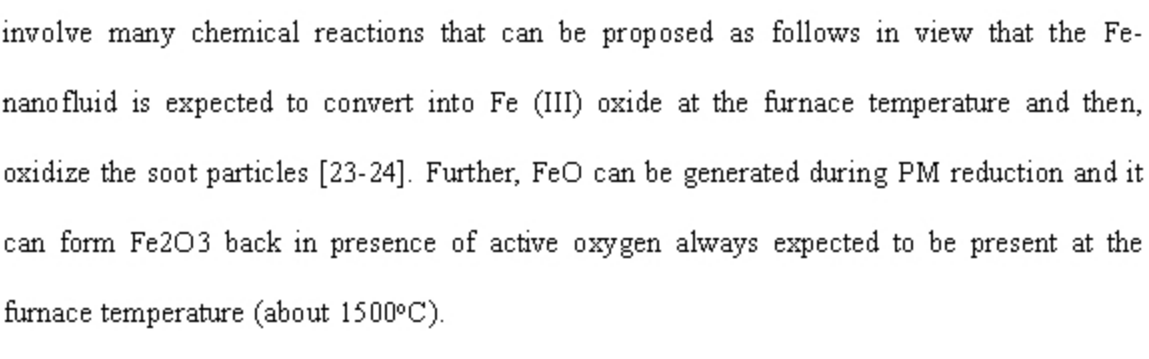


RESULTS AND DISCUSSION

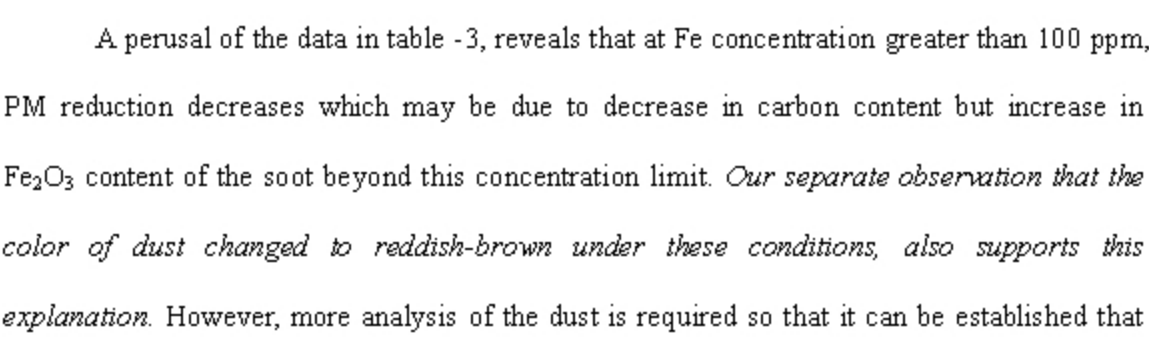
Preparation of Fe-nanofluid and the characteristics of heavy oil employed have already been discussed. The Fe-nanofluid is miscible with the heavy oil and can be mixed with it easily due to the already chemisorbed oleic acid (organic part) on the iron (III) hydroxide particles and its affinity towards diesel. The results of the effect of Fe-nanofluid on content of flue gases in heavy fuel oil fired boiler are given in table - 3.

Fe additive (ppm)	CO ₂ (%)	CO (ppm)	SO ₂ (ppm)	NO _x (ppm)	PM (mg/100 cc)	NO _x reduction (%)	PM reduction (%)
0	14.9	145	210	23.8	53.4	0.5	48.5
30	4.0	2	145	210	21.2	0.5	53.3
100	4.0	0	142	203	37.7	3.6	17.0
500	4.0	0	142	197	—	6.6	—

* Standard cubic meters worked out at 0°C and 1 atm.



As described in materials and methods, the % O₂ content in the gas was regulated by adjusting the combustion air flow and temperature. The burner, boiler and operational conditions were kept constant throughout the studies for combustion of heavy fuel oil with or without Fe-nanofluid fuel additive. Addition of Fe-nanofluid did not bring any significant change in CO, SO₂ and NO_x contents of flue gas (The PM reduction was optimum (53.3%) on addition of active metal (Fe) concentration of 100 ppm (by weight of heavy fuel oil used). The probable mechanism for PM reduction in the present case, may involve many chemical reactions that can be proposed as follows in view that the Fe-nanofluid is expected to convert into Fe (III) oxide at the furnace temperature and then, oxidize the soot particles [23-24]. Further, FeO can be generated during PM reduction and it can form Fe₂O₃ back in presence of active oxygen always existing to be present at the furnace temperature (about 1500°C).



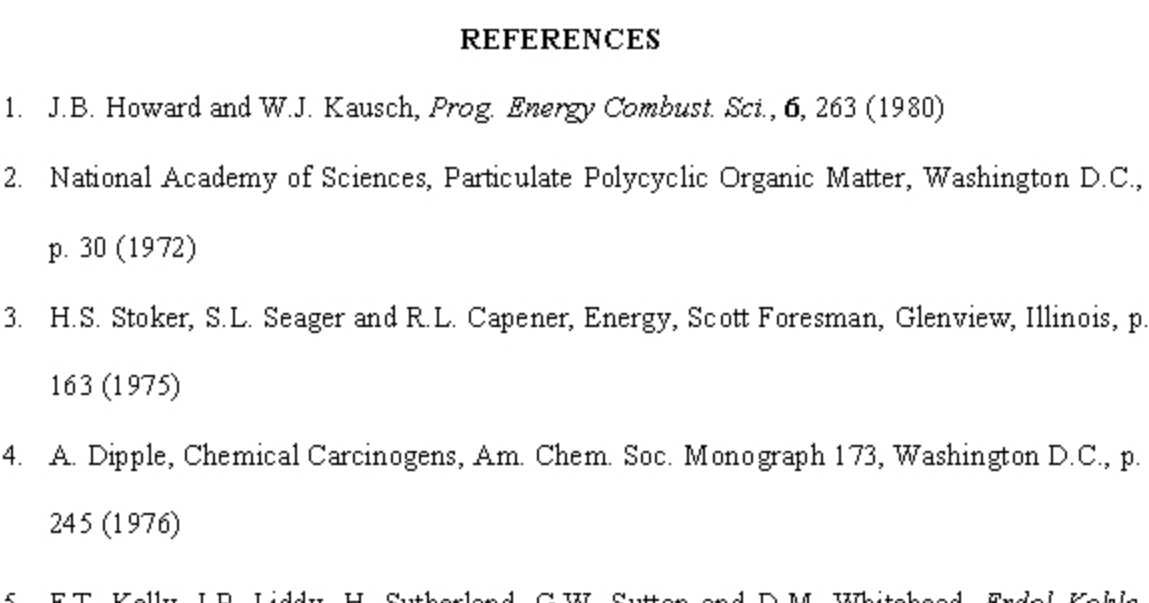
In this way the Fe-nanofluid is catalyzing the above given reactions and causing PM reduction. Besides this, Fe acts by getting occluded in soot particles, accelerating thereby the rate of its oxidation in O₂ rich flame zones [23].

A perusal of the data in table -3, reveals that at Fe concentration greater than 100 ppm, PM reduction decreases which may be due to decrease in carbon content but increase in Fe₂O₃ content of the soot beyond this concentration limit. Our separate observation that the color of soot changed to reddish-brown under these conditions, also supports this explanation. However, more analysis of the dust is required so that it can be established that carbon content of dust decreases further when the Fe concentration is increased over 100 ppm.

The additive did not bring any significant reduction in SO₂ content also. Further, almost no change in CO content was noticed that may be due to its conversion into CO₂ during the reactions proposed above. On increasing the metal concentration beyond 100 ppm, the PM reduction was found to decrease due to which experiments were not performed by taking more concentrations of the metal. However there was no significant effect on NO_x reduction which is desired for avoiding the trade-off between PM and NO_x emission which otherwise requires complex methodology as reported by earlier workers [1]. Therefore, the methodology and additive developed by us becomes significant as the additive investigated by us is easy to prepare and use for PM reduction in heavy fuel oil-fired boilers.

In our earlier reports [30, 31], we have proposed this additive as precursor for NO_x reduction too. Therefore it is necessary to explain the insignificant effect of Fe-nanofluid additive on NO_x reduction. When carbon is oxidized to CO₂, the O₂ is consumed and its content in the flue gas is expected to decrease. As already mentioned in present communication, the rate of flow of input combustion air was adjusted changed during the experiments under consideration to observe 4% O₂ in flue gas. Therefore, the air supply has been increased in

this experiment that might have supported more NO_x formation via reaction between N₂ and active oxygen. On the other hand, the increased NO_x would have reacted with active metal formed from Fe₂O₃ as reported by earlier workers [30-34]. It can also react with FeO formed during PM reduction processes already suggested in this paper. These three processes might have balanced the NO_x reduction to some extent and therefore, NO_x reduction was apparently non-significant as indicated by the experimental data (table-3).



However, the results also indicate that the additive may be tried for NO_x reduction in similar systems by using higher concentrations of Fe metal and more work is required in this direction.

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