Asian Journal of Chemistry Vol. 20, No. 7 (2008), 5767-5775

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

D.C. KIM, J.H. KIM, J.K. WOO, D.H. SHIN, Y.S. LEE† 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

Preparation and utilization method of a new Fe-nanofluid based heavy fuel oil additive for particulate matter 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 particulate matter by 53.3 % at an active metal concentration of 100 ppm without affecting the NOx content of flue gas significantly-a condition that is desirable for avoiding the trade-off between particulate matter and NOx emission which otherwise requires complex methodology. Proper explanations for the effects including the mechanism and reactions involved have also been discussed.

Key Words: Iron-Nanofluid, Heavy fuel oil, Boiler facility, Additive.

INTRODUCTION

Soot or particulate matter becomes black smoke when present in sufficient particle size and quantity in exhaust gases resulting from incomplete combustion of hydrocarbon fuels. Generally particulate matter is composed of about 50 % carbon and 50 % SiO_2. In low efficiency furnaces, the former is comparitively higher and later is lower while it is reverse case for the high efficiency furnaces. The size of particulate matter particles makes its ingestion deep into the lungs and the polynuclear aromatic hydrocarbons absorbed on particulate matter particles can cause cancer due to which stricter emission limits have been proposed[1-4]. The trade-off between particulate matter and NOx emission should be avoided and it requires complex methodology[5]. Therefore, such fuel additives are required that can reduce particulate matter without affecting NOx emission[6]. The metals manganese,

†Techno Bio Ltd., Kyeongki-do, Republic of Korea.
‡Permanent address: Department of Chemistry, Gurukul Kangri University, Haridwar-249 404, India.

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[1]. 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[7-11]. High atmospheric concentration of these oxides results in chronic manganese poisoning, manganic 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 explored extensively in animal feeding studies which show almost absence of toxicity although high concentration of iron oxides can cause irritation[14].

Ferrocene (dicyclopentadienyl iron) has been found to be the most effective particulate matter reduction additive in oil heating combustors in the utility and domestic boilers, in comparison to napthenates[15] of Ni, Co, Mn, Pb and Mg. 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 sulphonate[18]. Transition metal complexes having 20 % Fe and 25 % Mn were found to be most effective for particulate matter reduction in oil fired domestic boilers[1]. Seven most effective affective additives based on Fe, Mn, Ca and Co were found by Martin *et al.*[19] to cause 53-69 % particulate matter 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 particulate matter reduction[1]. Methylcyclopentadienyl manganese tricarbonal (MMT) has been found to be good particulate matter reduction agent in boilers[7], although it increases the particulate matter in cleaner combustors[8] 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 ºC and thus helps in particulate matter reduction[20]. Ba acts by different mechanism than Mn or Fe(III) as only it shows significant particulate matter reduction in primary zone flame radiation[21,22]. Fe acts by getting occluded in soot particles, accelerating thereby the rate of oxidation in O_2 rich flame zones[23]. Also the metal oxides are formed which remove carbon of the soot by changing it into CO, general reaction is suggested:

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

(M = Mn, Fe, Co and Ni)

Mitchell *et al.*[24-26] investigated the role of ferrocene, ferrocene derivatives and other organometallic compounds of Fe, Zn and Ti in particulate matter 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[24-26]. Out of various compounds investigated, 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)[26]. The reactions suggested for the action of ferrocene[26] are,

$$2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2$$

$$FeO + C \longrightarrow Fe + CO$$

Witzel *et al.*[6] reported the particulate matter 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 % particulate matter 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 by lowering the ignition temperature, it allowed 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. In recent reports Ma *et al.*[28] reported the 35.0-40.7 % soot reduction by 1-4 % concentration of eight organometallic compounds of Ba, Fe (including ferrocene), Cu, Mn, Ce in diesel engine. Guru *et al.*[29] 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.

In present communication, we have reported the preparation of a new Fe-nanofluid containing $Fe(OH)_3$ in diesel starting from industrial waste containing $FeSO_4 \cdot 7H_2O$ and the studies on particulate matter 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 Fe_2O_3, which is effective for particulate matter reduction. 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 in O_2 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.

EXPERIMENTAL

Smoke tube type boiler based on combustion of heavy oil was used. The experimental set up for the same is shown in Fig. 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. Gun type oil pressure burner was used. Preheating time was 1 h. The fuel oil atomizing temperature and atomizing pressure were maintained at 150 ºC and 22 Kg/cm^2, respectively. Rate of flow of heavy oil (fuel consumption) was maintained at 10 Kg/h giving a net load factor of 72.54 %. The rate of flow of input combustion air and heating were controlled to observe 4 % O_2 and temperature 340 ºC respectively in flue or stack gas.

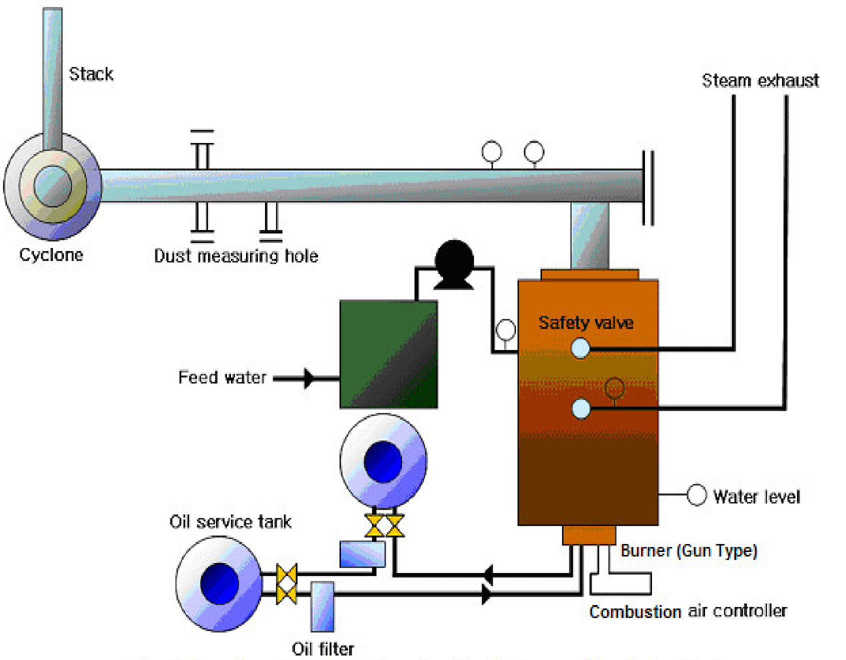

Fig. 1. Experimental setup of combustion boiler used for dust reduction

For collecting the samples of dust from flue gas, the Stack Gas sampling system (model sampling train, 5/17/23) of Clean Air Express (USA) was employed. The particulate matter samples were analyzed by weighing after collecting in Thimble filter tubes and drying at 200 ºC for 1 h. Thimble filters (88R, 25 mm × 90 mm) were procured from Toyo Roshi Kaisha Ltd., Japan.

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

TABLE-1
ANALYSIS OF THE HEAVY FUEL OIL USED FOR COMBUSTION BOILER

Content	C	H	N	S	O	Ash	Water*
% (W/W)	86.7	11.8	0.31	0.27	0.1	0.01	0.05

*% (V/V).

TABLE-2
PROPERTIES OF HEAVY FUEL OIL USED FOR COMBUSTION BOILER

Calorific value (K cal/Kg)	Specific gravity 15/4 ºC	Viscosity 50 ºC, SFS	Boling point (ºC)
10677	0.919	59	> 212

Preparation and analysis of Fe-nanofluid additive: Doubly distilled water was used for preparation of solutions and washing. All other chemicals used were Sigma Aldrich AR grade. The Fe-nanofluid was prepared by reported method[30]. 80 g of $FeSO_4·7H_2O$ (90.65 % purity, procured as industrial waste product from Cosmo Chemical Co. Ltd., Incheon, Republic of Korea) was mixed with 500 g water and 20 g of 30 % H_2O_2 solution was added and stirred for 45 min. Exothermic reaction takes place, in which $Fe_2(SO_4)_3$ was formed. 20 g NaOH was dissolved in 2 L water separately to maintain pH 13-14 and mixed slowly with $Fe_2(SO_4)_3$ solution and stirred at about 450 rpm for 0.5 h maintaining the pH between 10-12 (High speed mixer and pH meter used were Gawo tech TLS 250 and Hanna HI-8424 make, respectively). Brown coloured precipitate of $Fe(OH)_3$ was obtained and the solution was kept for about 12 h to allowed the precipitate settled down. The precipitate was washed with 2 L of water. 1 L water was added to precipitates and stirred with 30 mL of oleic acid for 45 min at 20-30 ºC for chemisorption of oleic acid molecules on $Fe(OH)_3$ particles. Now, 1 L diesel was added and stirring continued for further 0.5 h. After allowing the sedimen-tation for 2-3 d, 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 coloured 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 make). For particle size analysis, Microtrac particle size analyzer model Nanotrac NPA250 was used. The analysis revealed that this Fe-nanofluid contained 1.69 % Fe and average particle size of 22.48 nm (Fig. 2).

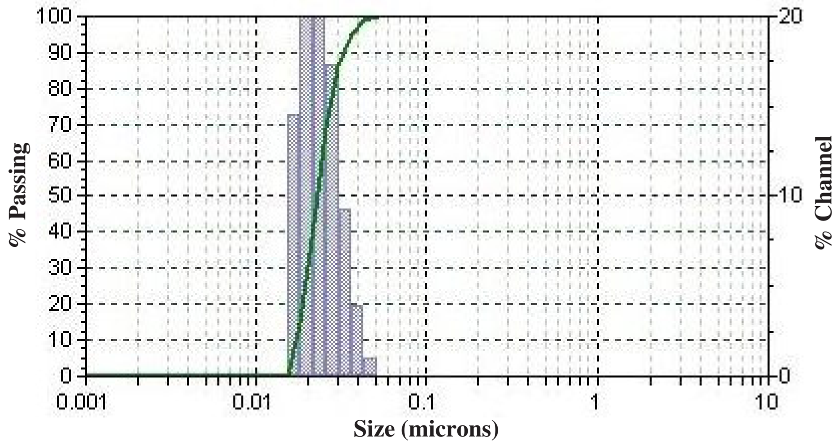

Fig. 2. Particle size analysis for $Fe(OH)_3$ nanofluid

RESULTS AND DISCUSSION

Preparation of Fe-nanofluid and the characteristics of heavy oil employed have 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.

TABLE-3
EFFECT OF Fe-NANOFLUID ADDITIVE ON VARIOUS CONTENTS OF FLUE GAS FROM HEAVY OIL FIRED COMBUSTION BOILER

Fe (ppm)	O_2 (%)	CO (ppm)	Sox (ppm)	NOx (ppm)	PM (mg/ *Sm^3)	NOx reduction (%)	PM reduction (%)
No additive	4.0	2	146	211	45.4	–	–
30	4.0	2	145	210	23.4	0.5	48.5
100	4.0	0	145	210	21.2	0.5	53.3
500	4.0	0	142	203	37.7	3.8	17.0
1000	4.0	0	143	197	–	6.6	–

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

The data for the effect of additive on particulate matter reduction is depicted graphically in Fig. 3.

As described in materials and methods, the % O_2 content in flue gas was regulated by adjusting/changing the combustion air flow and temperature. The burner, boiler and operational conditions were kept constant throughout

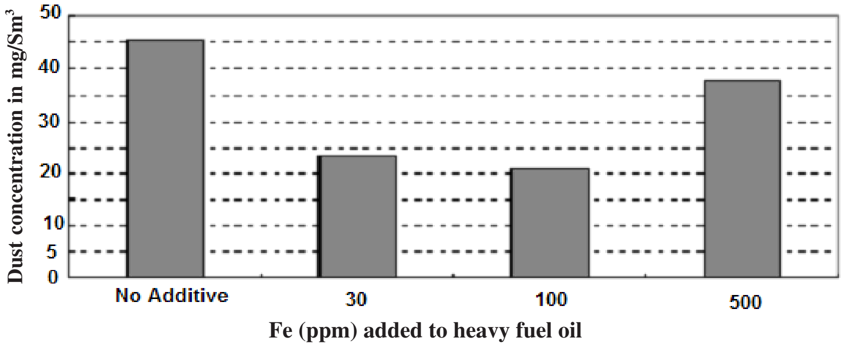

Fig. 3. Effect of Fe-nanofluid on particulate matter reduction

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, SOx and NOx contents of flue gas. The particulate matter 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 particulate matter 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[23,26]. Further, FeO can be generated during particulate matter reduction and it can form Fe_2O_3 back in presence of active oxygen always expected to be present at the furnace temperature (about 1500 ºC).

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

In this way, the Fe-nanofluid is catalyzing the above given reactions and causing particulate matter reduction. Besides this, Fe acts by getting occluded in soot particles, accelerating thereby the rate of its oxidation in O_2 rich flame zones[23].

A perusal of the data in Table-3, reveals that at Fe concentration greater than 100 ppm, particulate matter reduction decreases which may be due to decrease in carbon content but increase in Fe_2O_3 content of the soot beyond this concentration limit. The separate observation that the colour of dust 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 SOx content also. Further, almost no change in CO content was noticed that may be due to its conversion into CO_2 during the reactions proposed above. On increasing the metal concentration beyond 100 ppm, the particulate matter 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 NOx reduction which is desired for avoiding the trade-off between particulate matter and NOx emission which otherwise requires complex methodology as reported by earlier workers[5]. Therefore, the methodology and additive developed by us becomes significant as the additive investigated by us is easy to prepare and use for particulate matter reduction in heavy fuel oil-fired boiler facilities.

In our earlier reports[30,31], we have proposed this additive as precursor for NOx reduction too. Therefore, it is necessary to explain the insignificant effect of Fe-nanofluid additive on NOx reduction. When carbon is oxidized to CO_2, the O_2 is consumed and its content in 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 % O_2 in flue gas. Therefore, the air supply has been increased in this experiment that might have supported more NOx formation *via* reaction between N_2 and active oxygen. On the other hand, the increased NOx would have reacted with active metal formed from Fe_2O_3 as reported earlier[30-34]. It can also react with FeO formed during particulate matter reduction processes already suggested in this paper. These three processes might have balanced the NOx reduction to some extent and therefore, NOx reduction was apparently non-significant as indicated by the experimental data (Table-3).

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

However, the results also indicate that the additive may be tried for NOx reduction in similar systems by using higher concentrations of Fe metal and more 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 thankful to Korean Federation of Science and Technology Societies for invitation as Brain Pool Scientist for undertaking the research work in this communication.

REFERENCES

1. J.B. Howard and W.J. Kausch, *Prog. Energy Combust. Sci.*, **6**, 263 (1980).
2. National Academy of Sciences, Particulate Polycyclic Organic Matter, Washington DC, p. 30 (1972).
3. H.S. Stoker, S.L. Seager and R.L. Capener, Energy, Scott Foresman, Glenview, Illinois, p. 163 (1975).
4. A. Dipple, Chemical Carcinogens, Am. Chem. Soc. Monograph 173, Washington DC, p. 245 (1976).
5. F.T. Kelly, J.P. Liddy, H. Sutherland, G.W. Sutton and D.M. Whitehead, *Erdol Kohle. Erdgas. Petrochem.*, **42**, 408 (1989).
6. L. Witzel, P. Moszkowicz and G. Claus, *Fuel*, **74**, 1881 (1995).
7. G.B. Martin, D.W. Pershing and E.E. Berkau, U.S. EPA, Office of Air programs, RTP, Pub. No. AP-87 (1971).
8. D.B. Giovanni, P.G. Pagni, R.F. Sawyer and L. Hughes, *Comb. Sci. Tech.*, **6**, 107 (1972).
9. P.G. Pagni, L. Hughes and T. Novakov, NATO/AGARD meeting paper no. 25, London, NTIS no. AD769278 (1973).
10. S. Hersh, J.S. Hurley and R.C. Carr, Presented at Meeting of Air Pollution Control Association, Portland, Oregon (1976).
11. A.F. Klarman, Evaluation of Smoke Suppressant Fuel Additives for Jet Engine Test Cell Smoke Abatement, NAPTC-PE-103 (1977).
12. R.J. Sullivan, Air Pollution Aspects of Manganese and Its Compounds, National Air Pollution Control Administration, NTIS, PB 188 079 (1969).
13. R.J. Sullivan, Air Pollution Aspects of Barium and Its Compounds, National Air Pollution Control Administration, NTIS, PB 188 083 (1969).
14. R.J. Sullivan, Air Pollution Aspects of Iron and Its Compounds, National Air Pollution Control Administration, NTIS, PB 188 088 (1969).
15. R.L. Weeks, W.L. Clinkenbeard and J.D. Solties, Proc. Fifth World Petroleum Congress, section VI, p. 381 (1959).
16. R.J. Hartle and J.R. McGuire, US Patent, 3,082,071 (1963).
17. A.V. Churchill and E. Mitchell, US Patent, 2,971,828 (1961).
18. J.J. Vaerman, *J. Inst. Petrol.*, **50**, 155 (1964).
19. D.W. Pershing, G.B. Martin, E.E. Berkau and R.E. Hall, US EPA report no. EPA-650/2-73-031 (1973).
20. B.S. Chittawadge and A.N. Voinov, *Indian J. Technol.*, **3**, 209 (1965).
21. N.J. Friswell, in Emissions from Continuous Combustion Systems, Plenum Press, New York, p. 161 (1972).
22. M.W. Shayeson, SAE Paper no. 670866 (1967).
23. D.H. Cotton, N.J. Friswell and D.R. Jenkins, *Combust. Flame*, **17**, 87 (1971).
24. J.B.A. Mitchell, D.J.M. Miller and M. Sharpe, *Combust. Sci. Technol.*, **74**, 63 (1991).
25. J.B.A. Mitchell and D.J.M. Miller, *Combust. Flame*, **75**, 45 (1989).
26. J.B.A. Mitchell, *Combust. Flame*, **86**, 179 (1991).
27. P. Bonczyk, *Combust. Flame*, **51**, 219 (1983).
28. L.C. Ma and Y. Liu, *J. Fuel Chem. Technol.*, **34**, 230 (2006).
29. M. Guru, U. Karakaya, D. Altiparmak and A. Alicilar, *Energy Conver. Manag.*, **43**, 1021 (2002).
30. 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, pp. 601-603 (2008).
31. 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).
32. P.S. Fennel and A.N. Hayhurst, Poster 1-C05, 28th International Symposium on Combustion, Edinburgh, Scotland (2000).
33. A.N. Hayhurst and A.D. Lawrence, *Combust. Flame*, **110**, 351 (1997).
34. A.N. Hayhurst and Y. Ninomiya, *Chem. Eng. Sci.*, **53**, 1481 (1998).

(*Received*: 24 May 2008; *Accepted*: 5 June 2008) AJC-6605