

## Fluidized Bed Combustion of Residual Oils

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### INTRODUCTION

Shortage of crude oil plus the lack of progress in the development of stack gas clean up systems have sparked interest in processes that generate electric power by the fluidized bed combustion of residual oil and coal with high sulfur and nitrogen content. Many development works on the fluidized bed combustion of fossil fuels have been carried out by various organizations in U.S.A. and other countries. In all of these works, dolomite or limestone has been used as a bed material because these substances have ability to absorb  $H_2S$  or  $SO_2$  released during combustion. Furthermore, reduced  $NO_x$  emission can be achieved by the lower operating temperature in fluidized bed combustion than conventional combustors(1,2).

The authors have investigated the combustion of various residual oils in the fluidized bed of a dolomite at  $700 \sim 1000^\circ C$  and atmospheric pressure. By use of the dolomite, heavy residual oils of low reactivity such as an Arabian Light vacuum residue could be burnt with combustion efficiency higher than 98% above  $850^\circ C$ . It was also shown that the dolomite was effective to reduce the concentration of  $SO_x$  and  $H_2S$  in flue gases to very low levels at temperatures below  $900^\circ C$ . The purpose of the present work was to investigate catalytic reduction of  $NO_x$  (mostly fuel  $NO_x$ ) by ammonia using a fluidized bed of the dolomite loading various kinds of metal oxide.

### EXPERIMENTAL

Figure 1 shows a schematic diagram of the fluidized bed combustion system. The combustor was made of 50 mm  $\phi$  i.d. SUS 27 stainless steel tube and its bed depth was 400 mm. Stainless steel beads (3 mm  $\phi$ ) were packed at the conical-bottom of the combustor as bed support and gas distributor. Feed oil (Arabian Light vacuum residue) was introduced at the bottom of the fluidized bed through an atomizer from a microfeeder. To prevent coke plugging in the feed pipe, the atomizer was cooled by circulating a coolant. The bed material was first heated externally to a desired temperature in a stream of air and then the residual oil was fed. After combustion started, external heating was cut off. To remove the heat evolved, water was circulated in a coil of 6 mm  $\phi$  o.d. SUS 27 stainless steel tube which was immersed in the fluidized bed. After a certain period of combustion, ammonia was admitted to the combustion system at the upper level of fluidized bed from a cylinder which contained 5% ammonia in nitrogen.

After the condensation of steam in an ice-trap, the flue gas passed through a solution of 3% hydrogen peroxide to absorb  $SO_x$  and through a solution of ammine complex of zinc to absorb  $H_2S$ . The  $SO_x$  in the solution was titrated by barium acetate using Arsenazo III as an indicator. The  $H_2S$  concentration in the solution was determined by  $I_2$  titration using sodium thiosulfate. The flue gases were periodically sampled to determine their compositions. The  $NO_x$  concentrations were measured as nitrous ions by means of photometric analyzer using naphthyl ethylene diamine. Compositions of gaseous products, methane, carbon monoxide and dioxide were determined by means of gas chromatography.

Dolomite from Kuzuo (Tochigi Prefecture) was used after calcined at 700°C (CaCO<sub>3</sub>·MgO). Its composition (wt%) was as follows: CaO 65.4, MgO 33.4, SiO<sub>2</sub> 0.8, Al<sub>2</sub>O<sub>3</sub> 0.3, and Fe<sub>2</sub>O<sub>3</sub> 0.1. The dolomite was impregnated with an aqueous solution of Fe, Co, Cu, or Cr nitrate. These were finally calcined at 900°C prior to reaction.

#### RESULTS AND DISCUSSION

Table I shows the catalytic activity of some typical bed materials for the reduction of NO<sub>x</sub> emitted during combustion of the residual oil. The concentration of added NH<sub>3</sub> (1050 ppm) was calculated from the volume of flue gases (wet basis) and feed rates of ammonia. Combustion was carried out at the optimum operating conditions for the dolomite: bed temperature, 850°C; excess air, 20%; residence time, 0.57 sec. The concentrations of NO<sub>x</sub> in the absence of ammonia were almost independent of the kind of bed materials (near 320 ppm). The NO<sub>x</sub> concentrations decreased on addition of NH<sub>3</sub> to the combustion system. As shown in Table I, Fe<sub>2</sub>O<sub>3</sub>-dolomite was the most active among the bed materials tested.

Table I. Catalytic Activity of Some Bed Materials for the Reduction of NO<sub>x</sub> by NH<sub>3</sub>

	Dolomite	Fe <sub>2</sub> O <sub>3</sub> - Dolomite	CuO- Dolomite	Cr <sub>2</sub> O <sub>3</sub> - Dolomite	CoO- Dolomite
C(a)	328	305	313	348	303
C(b)	246	149	184	246	192
X (%)	25.0	51.1	41.2	29.3	36.6

C(a) and C(b) are the concentrations of NO<sub>x</sub> in flue gases in the absence and presence (1050 ppm) of ammonia, respectively. And X is % reduction of NO<sub>x</sub> defined by  $[C(a)-C(b)] \times 100 / C(a)$ . The content of metal oxides was 10 wt%.

Figure 2 shows the effect of bed temperature on the reduction of NO<sub>x</sub> by ammonia in the fluidized bed combustion using Fe<sub>2</sub>O<sub>3</sub>-dolomite containing 7.5 wt% of Fe<sub>2</sub>O<sub>3</sub>. When NH<sub>3</sub> was absent, the NO<sub>x</sub> emission increased with increasing bed temperature. The NO<sub>x</sub> emission, however, decreased in the temperature range of 700 ~ 950°C in the combustion with NH<sub>3</sub> added. The catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> was enhanced remarkably as the bed temperature increased. At 950°C, the NO<sub>x</sub> concentration was reduced from 337 to 116 ppm by the catalytic reduction with NH<sub>3</sub>.

Excess air was found to be a critical factor for the catalytic reduction of NO<sub>x</sub> on the Fe<sub>2</sub>O<sub>3</sub>-dolomite. With stoichiometric amount of air, the NO<sub>x</sub> concentration was not reduced by the addition of NH<sub>3</sub>. However, the NO<sub>x</sub> concentration decreased with increasing amount of excess air and it was leveled off at about 10% excess air.

Figure 3 shows the effect of NH<sub>3</sub> concentration on the NO<sub>x</sub> emission. The NO<sub>x</sub> concentration decreased with increasing concentration of added NH<sub>3</sub>. The lowest NO<sub>x</sub> emission of 57 ppm was attained when 2000 ppm NH<sub>3</sub> was added at 850°C, 10% excess air and 0.61 sec residence time.

Figure 4 shows that combustion efficiency was also improved by loading Fe<sub>2</sub>O<sub>3</sub> on the dolomite in the range of combustion temperature from 700 to 950°C. Here combustion efficiency was defined as percent carbon in the oil converted to carbon dioxide. Combustion efficiency increased with increasing bed temperature and reached 100% at 950°C on both bed materials. The Fe<sub>2</sub>O<sub>3</sub>-dolomite was more effective

for combustion at lower temperatures than the dolomite. Combustion efficiency also increased with increasing excess air and it exceeded 99% at 10% excess air without formation of carbon monoxide and methane.

Figure 5 shows the effect of bed temperature on the emission of SOx and H<sub>2</sub>S during combustion in the fluidized bed of the Fe<sub>2</sub>O<sub>3</sub>-dolomite. The results on the dolomite fluidizing were also shown in Figure 5. Concentrations of (SOx + H<sub>2</sub>S) in flue gases were as low as 10 ppm in the temperature range of 700 ~ 900°C but they increased abruptly as the bed temperature further increased as described by Moss (3) and Roberts (4). The mode in variation of (SOx + H<sub>2</sub>S) emission with bed temperature in the Fe<sub>2</sub>O<sub>3</sub>-dolomite and the dolomite bed were similar. This suggests that the sulfur removing efficacy of the Fe<sub>2</sub>O<sub>3</sub>-dolomite is completely due to the dolomite.

#### CONCLUSION

The concentration of NOx emitted during the combustion of the vacuum residual oil was reduced when NH<sub>3</sub> was added to the fluidized bed of Fe<sub>2</sub>O<sub>3</sub>-dolomite. Furthermore, combustion efficiency higher than 99% was attained above 800°C. Simultaneously concentrations of (SOx + H<sub>2</sub>S) in the flue gases were kept at very low level by the action of dolomite which might absorb SOx and H<sub>2</sub>S. The optimum operating conditions for the Fe<sub>2</sub>O<sub>3</sub>-dolomite fluidized bed were determined as follows: bed temperature, 850°C; excess air, 10%; residence time, 0.61 sec. Under these conditions, the concentrations of (SOx + H<sub>2</sub>S) and NOx were as low as 10 ppm and 57 ppm, respectively.

#### REFERENCES

- (1) Nack, H., Kiang, K.D., Liu, K.T., Murthy, K.S., Smithson, G.R., and Oxley, J.H., Int. Fluid. Conf. (U.S.A.) 2, 339 (1976).
- (2) Beer, J.M., Sym. Int. Combust. (U.S.A.) 16, 439 (1977).
- (3) Moss, G., Int. Conf. Fluid. Combust. D2-1 (1975).
- (4) Roberts, A.G., Stantan, J.E., Wilkins, D.M., Beacham, B., and Hoy, H.R., Int. Conf. Fluid. Combust. D4-1 (1975).

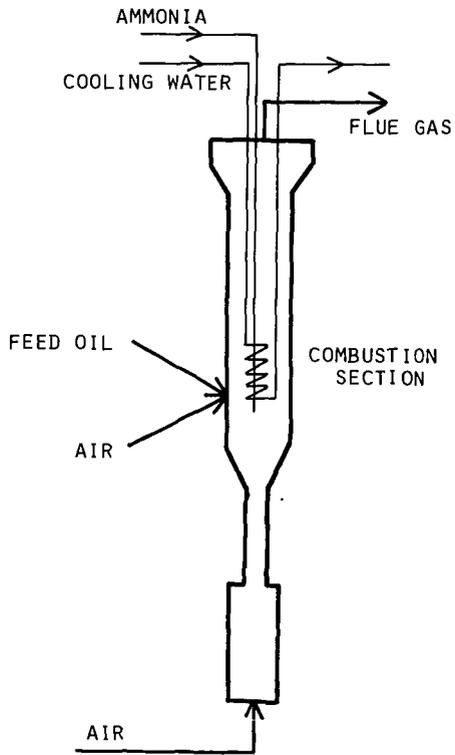
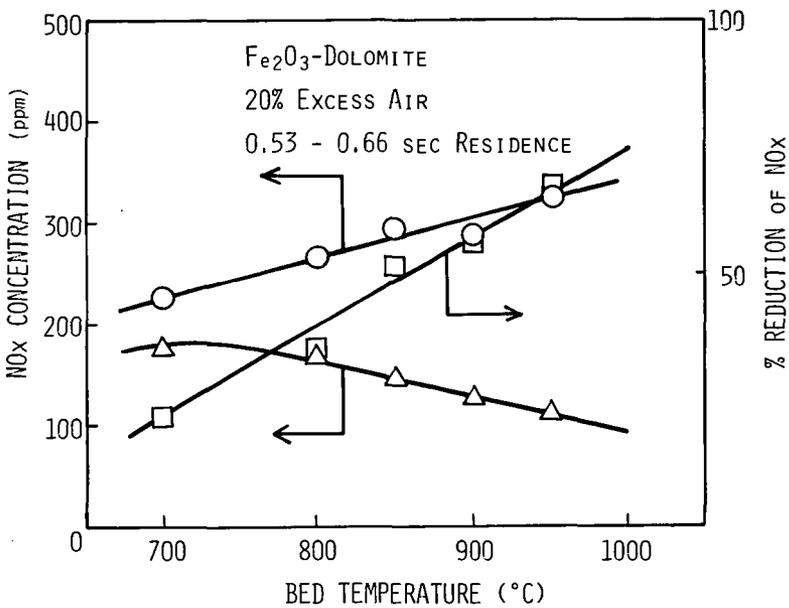


Figure 1. Diagram of Combustor Assembly



- IN THE ABSENCE OF AMMONIA
- △ IN THE PRESENCE OF AMMONIA (1050 ppm)
- % REDUCTION OF NO<sub>x</sub>

Figure 2. The Effect of Bed Temperature on the Reduction of NO<sub>x</sub> by NH<sub>3</sub>.

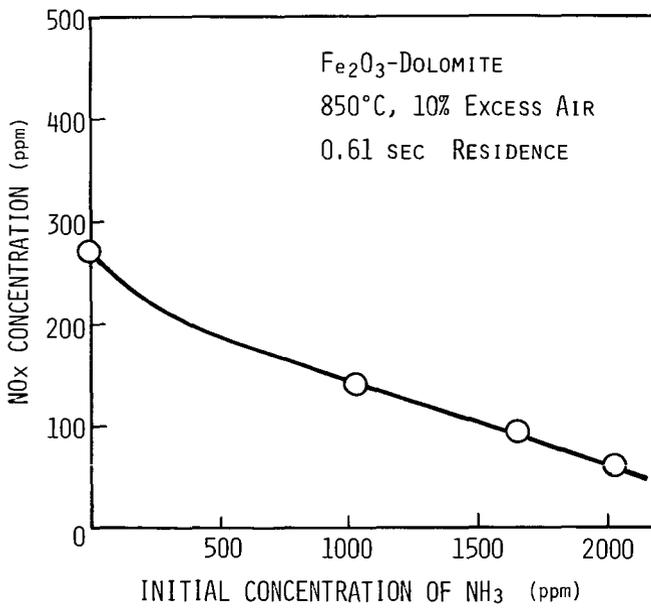


Figure 3. The Effect of NH<sub>3</sub> Concentration on the Reduction of NO<sub>x</sub> by NH<sub>3</sub>.

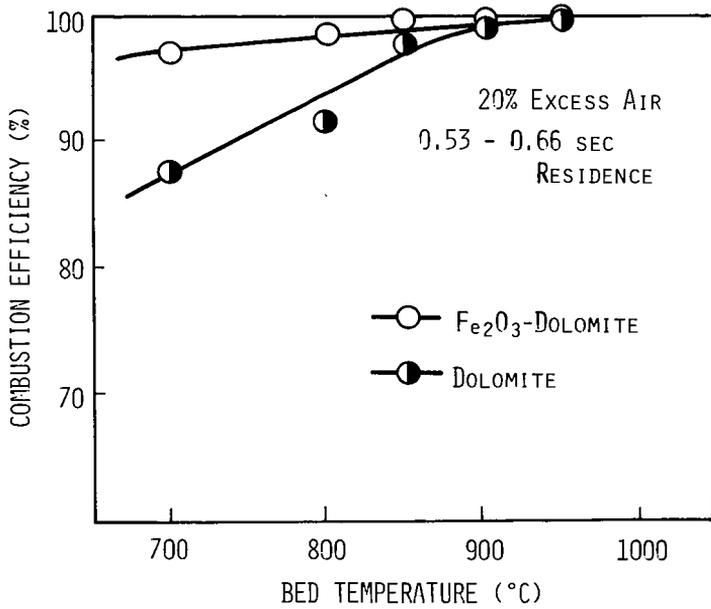


Figure 4. Relationships between Combustion Efficiency and Bed Temperature

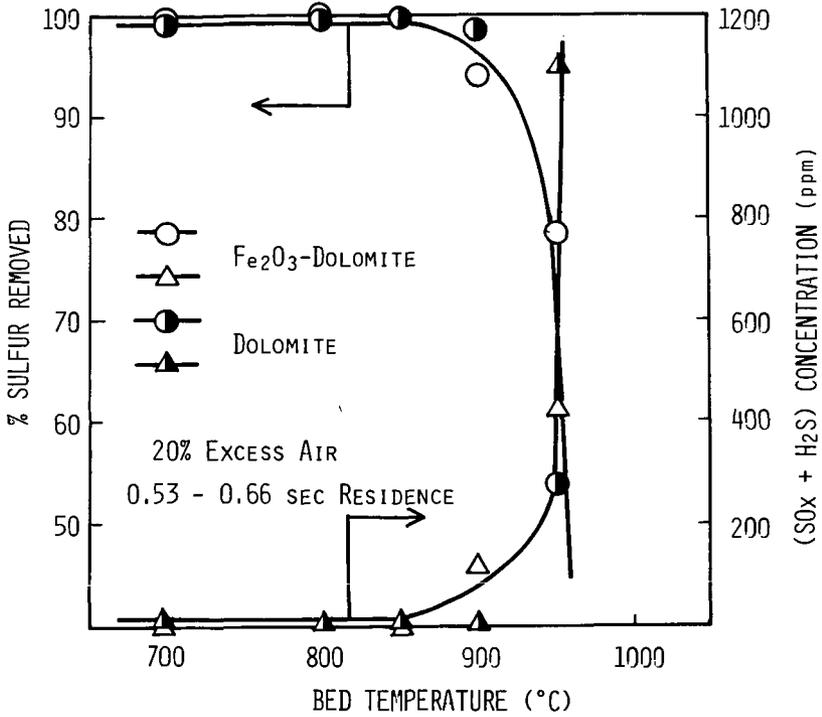


Figure 5. Sulfur Removing Efficacy of  $\text{Fe}_2\text{O}_3$ -Dolomite and Dolomite as a Function of Bed Temperature.