

Reduction of Nitrogen Oxide Emission of a Medium-Pressure Boiler by Fuel Control

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Abstract

A study of reducing nitrogen oxide (NO) emission by using different fuel oil/hydrogen-rich refinery gas ratios (FO/RG) of the volumetric flow rate in a 130-ton/hr, full-scale, medium-pressure boiler was carried out. The influence of the FO/RG ratio on boiler outlet temperature, flue -gas flow rate and temperature, and O₂ concentration in the excess air was also investigated. Test results show that by adjusting the FO/RG volumetric flow rate ratio from 5:1 to 1.8:1, fuel cost was reduced by as much as \$33 million NT (~\$1.1 million US) per year. Concentration of NO was lowered from 167 to 152 ppm, reducing NO emission a total of 72 tons per year. The air pollution fee was cut as much as \$860,000 NT (~\$27,000 US) each year. Hence, changing the FO/RG ratio of the volumetric flow rate can not only save fuel costs, but can also greatly reduce NO emission and air pollution fees. Results of this study can help to develop boilers that operate more economically and efficiently.

Keywords: nitrogen oxide, flue gas, air pollution control, FO/RG ratio

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INTRODUCTION

To control the emission of NO_x effectively, we must first understand its formation mechanism. The formation reaction mechanism of nitrogen oxides are categorized into Thermal NO_x , Fuel NO_x and Prompt NO_x (Bittner et al., 1994; Kokkinos, 1994). Based on Zeldovich's Mechanism, the formation of thermal NO_x is mainly initiated by free radicals as nitrogen, oxygen and OH which come from the destruction of gaseous molecules under the heat released during combustion at high temperature ($>1,300^\circ\text{C}$) (Kokkinos, 1994; Sloss et al., 1992). Those active substances react further with other gaseous molecules to form NO_x . Fuel NO_x mainly comes out of the combustion of nitrogen molecules contained in the fuel under oxidized conditions. Regarding Prompt NO_x , at the fuel-rich area of the flame zone, hydrocarbon decomposes to CH free radical and reacts with nitrogen in the air to form HCN. Then, HCN will react through the reaction path of thermal NO_x to increase the formation of NO_x (Sloss et al., 1992; Hill and Smoot, 2000). Fig. 1 is a graphical representation of the mechanistic pathways leading to NO_x formation.

The formation mechanism of NO_x is complicated and there are many influential variables such as fuel type, N/H content in the fuel, temperature, residence time of air at the high-temperature area, air/fuel ratio, and operation conditions. The treatment techniques are categorized into three groups: pretreatment before combustion, treatment during combustion (process modification), and after-treatment following combustion (Kokkinos, 1994; Sloss et al., 1992; Konnov, et al., 2001). Pretreatment methods include fuel switching, fuel de-nitrification, fuel additive, etc.

Treatment during combustion is done mainly by modifying the existing combustion process; for example, by reducing the combustion temperature, which brings down both O_2 concentrations in the main combustion area and combustion air flow rate. This diminishes the formation of both thermal NO_x and prompt NO_x . Other techniques include low excess air (LEA), staged combustion air (SCA), low NO_x burner (LNB), fuel-gas recirculation (FGR), etc. (Kokkinos, 1994; Bozzuto et al., 1994; Rest et al., 1999).

The technique of after-treatment, the so-called flue-gas De-nitrification (DE- NO_x), is to treat the NO_x formed in flue gas during combustion. It mainly includes selective non-catalytic reduction (SNCR), non-selective catalytic reduction (NSCR), selective catalytic reduction (SCR), non-catalytic reduction (NCR), etc. (Sloss et al., 1992; Rest et al., 1999).

Previous studies show that adding different ratios of hydrogen in the fuel gas (including natural gas, propane and n-heptane) leads to the reduction of Prompt NO volume yielded. The higher the H_2 content, the lower the yield of Prompt NO , as well as the CO concentration. In addition, the concentration and emission of soot reduces as the H_2 content increases. This is because H_2 provides the flame with lower carbon concentration, while CO and soot influence the transition of radiation heat. As a consequence, the increase of H_2 content reduces the loss of radiation heat (Naha et al., 2004; Choudhuri et al., 2000; Gollahalli et al., 2003; Tseng, 2002).

In the study, the commonly used refinery gas (RG) was replaced with surplus hydrogen-rich, fuel gas, which is waste resulting from the production process that is disposed of by burning. The test was conducted using a 130-ton/hr full-scale medium-pressure steam boiler to find the optimized operating model. The objective was to evaluate the effect of using surplus gas on the reduction of air emission, as well as to show any potential energy-cost savings. Generally speaking, treatment during combustion (process modification) cost less than treatment after combustion, which lowered overall operation costs.

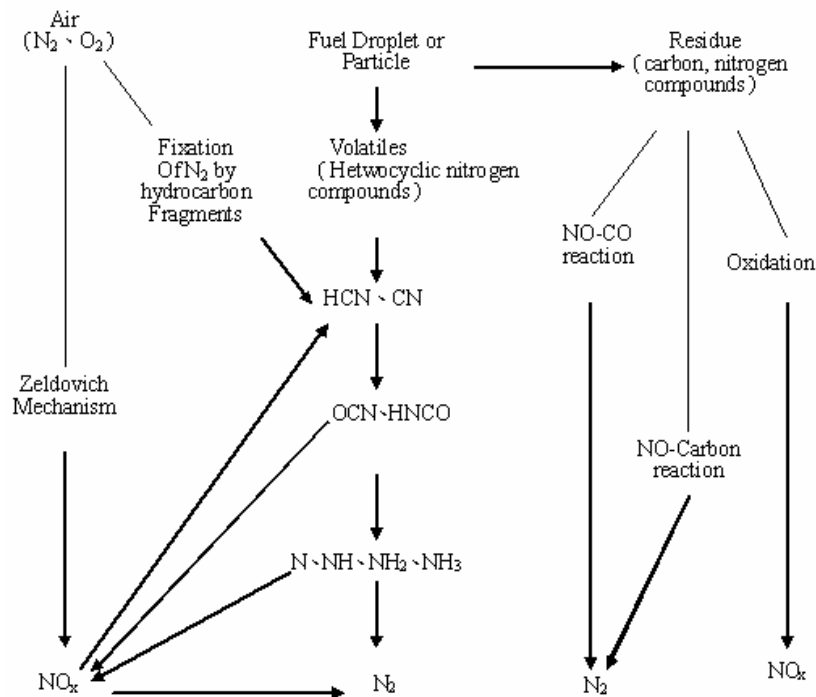


Fig. 1. Formation of Nitrogen Oxides in Fossil Fuel Combustion Mechanistic Pathways (Angelos Kokkions, 1994).

EXPERIMENTAL SECTION

The dimensions of the boiler used in this study was 6.7m (L) x 4.8m (W) x 8.9m and the operating pressure was about 20 kg/cm². Four burners were located inside the boiler, with two on the upper layer and two on the lower.

Both fuel oil and fuel gas were mixed together for use in the combustion process. Fuel Oil No. 6 was used, which contains: (wt %) C = 86.03%, H = 12.5%, S = 0.5%, N = 0.35%, O = 0.625%, and ash = 0.05%. The fuel gas was the hydrogen-rich surplus yielded from the production process, which is considered to have no economic value as a waste product. The average amount of ingredients included: CH₄ = 13.1%, C₂H₆ = 8.0%, C₂H₄ = 3.0%, C₃H₈ = 3.3%, C₄⁺ = 2.1%, C₅⁺ = 0.5%, C₆⁺ = 0.2%, H₂ = 70.01%, H₂S = 180 ppmv. A continuous emission monitor system

(CEMS) (E.S.A MIR 9000) was employed to conduct the on-line analysis of nitrogen oxides by recording the concentration of ingredients in the flue gas. The boiler was operated by an automatic combustion control system (ACC) (see schematic diagram in Figure. 2).

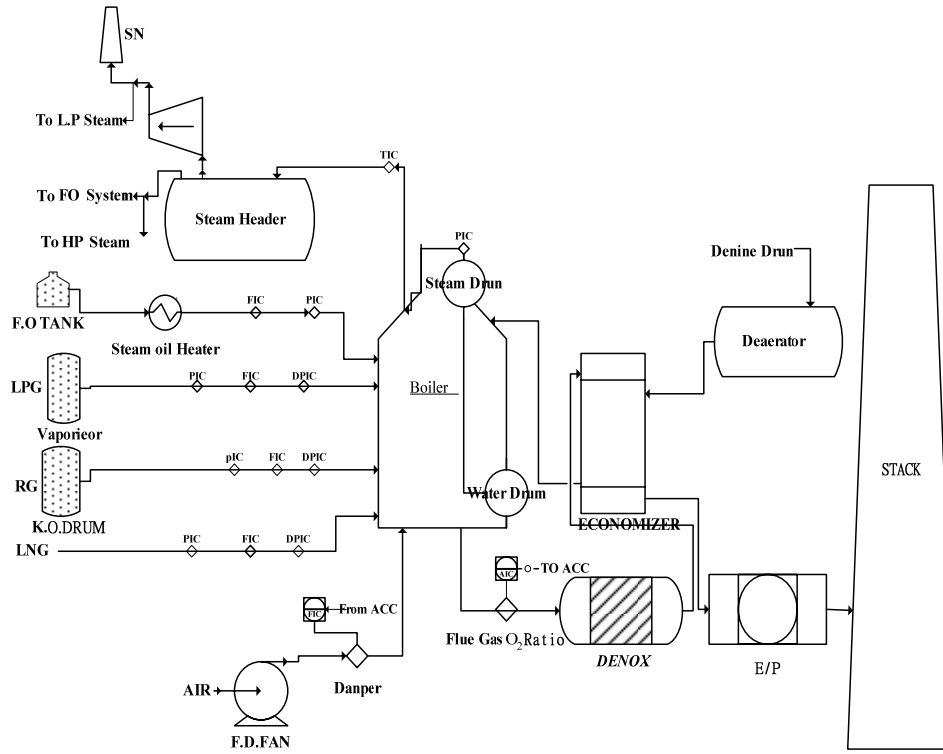


Fig. 2. Schematic diagram of the boiler.

When the boiler's energy system became unstable and resulted in changes of steam pressure, the system would automatically adjust both the fuel-feeding quantity and the volume of air. The fuel and air were kept at a constant fuel/air ratio to ensure complete combustion by controlling the fuel valve and the inlet, or the blower speed (Bebar et al., 2002). To ensure the accuracy of the test results, the calibration of both the ash-blowing and the flue-gas automatic-detection instruments was completed before the experiment took place.

RESULTS AND DISCUSSION

The emission quantity of NO_x is related to both the thermodynamics of the combustion process (i.e., temperature and air/fuel ratio) and the combustion burner. Therefore, in order to reduce the NO_x emission, it is more effective to control the operational variables of the combustion process than to replenish control equipment (air pollution control devices, APCDs). To find out the impact of FO/RG, two different volumetric flow-rate ratios were applied in this study with full-

scale plant measurement: one with the FO/RG volumetric flow-rate ratio at 5:1 and the other at 1.8:1. The rate of the steam-producing quantity and O₂ concentration in excess air was kept the same as the operation conditions. The test results are shown as Fig. 3.

Fig. 3 shows that at the FO/RG volumetric flow rate ratio of 5:1 and the boiler steam generating rate of between 84 and 94 ton/hr, the average amount of NO formed was 167 ppm, while the FO/RG volumetric flow-rate ratio of 1.8:1 averaged 152 ppm of NO. The result indicates that by adjusting the 5:1 ratio to 1.8:1, the volume of NO yielded can be reduced by 15 ppm or 8.5%. The higher NO concentration under the 5:1 ratio was due to the fact that the fuel oil contained more nitrogen compound: therefore, more fuel oil used the more NO yielded.

Fig. 4 shows that with the FO/RG volumetric flow rate ratio of 1.8:1, the average temperatures at the boiler outlet and the flue duct were 321 °C and 148.8 °C, respectively. At the 5:1 ratio, the average temperatures were 302 °C and 146.5 °C, respectively. The reasons why the temperature was lower with 1.8:1 flow-rate ratio are as follows:

- (1) As the flame luminosity of the fuel gas was lower than that of the fuel oil, the furnace chamber absorbed less heat; hence, resulting in a higher temperature at both the boiler outlet and the flue duct.
- (2) The fuel gas used in the test contained more water than the fuel oil did, which resulted in the rise of radiation heat absorbed at the convection heating surface zone. As a consequence, more heat was absorbed at the heat-recovery zone, which led to higher temperatures at the outlets of both the boiler and the flue duct.

Gaseous Fuels:

$$\text{Volume Cp}^+/\text{Volume Fuel} = (\%CO \times 0.0289) + (\%H_2 \times 0.0289) + (\%CH_4 \times 0.1056) + (\%C_2H_6 \times 0.1823) + (\%C_3H_8 \times 0.259) + (\%C_4H_{10} \times 0.3357) + (\%inters^* \times 0.01) - (\%O_2 \times 0.0378) + (\%XSA/100) \times 0.0239 \times \theta \quad (1)$$

Liquid Fuels:

$$m^3 \text{ Cp}^+/\text{kg (fuel)} = (\%C \times 1.508) + (\%H \times 5.433) + (\%S \times 0.5650) + (\%CO_2^\oplus \times 0.0861) + (\%H_2O^\ominus \times 0.2104) + (\%N \times 0.1353) - (\%O^\square \times 0.4477) + (\%XAS/100) \times [(\%C \times 1.508) + (\%H \times 4.493) + (\%S \times 0.5650) - (\%O^\square \times 0.5662)] \quad (2)$$

where

inters* include CO₂, N₂, SO₂, SO₃, argon, helium, and other non-combustibles.

Cp⁺ = combustion products (flue gas)

$$\theta = \%CO + \%H_2 + (4 \times \%CH_4) + (7 \times \%C_2H_6) + (10 \times \%C_3H_8) + (13 \times \%C_4H_{10}) - (2 \times \%O_2)$$

⊕ = If %C includes the unavailable carbon already in the form of CO₂, the CO₂ term should be omitted and note [⊖] observed.

⊖ = If %H includes the unavailable hydrogen already in the form of H₂O, this H₂O term should be omitted and note [⊕] observed.

⊖ = These equations may be used for gaseous fuels containing no CO. If the values substituted in the above equations for %C, %H, and %S are the percentages of total carbon, hydrogen, and sulphur (available plus unavailable), then the %O should be the total (free and combined) oxygen. If the values substituted in the above equations for %C, %H, and %S are the percentages of available carbon, hydrogen and sulfur, respectively, then the %O should be the free oxygen.

XSA = excess air

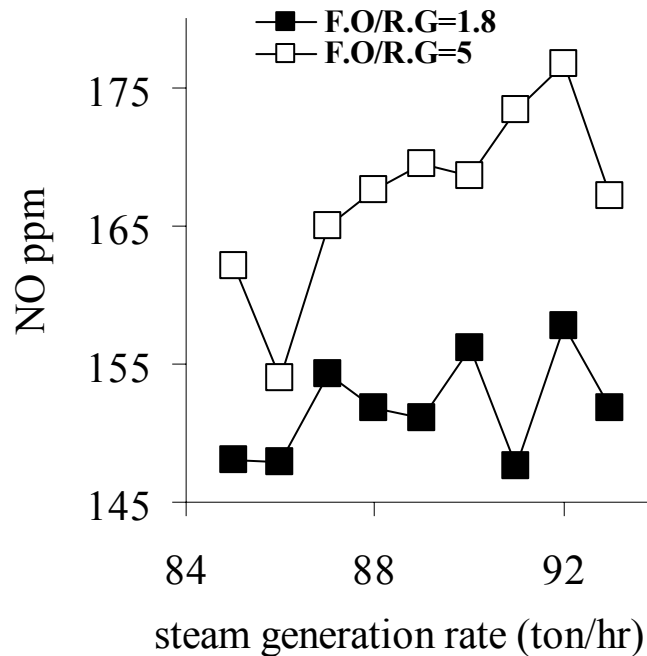


Fig. 3. Relationship between the steam generation rate and NO concentration.

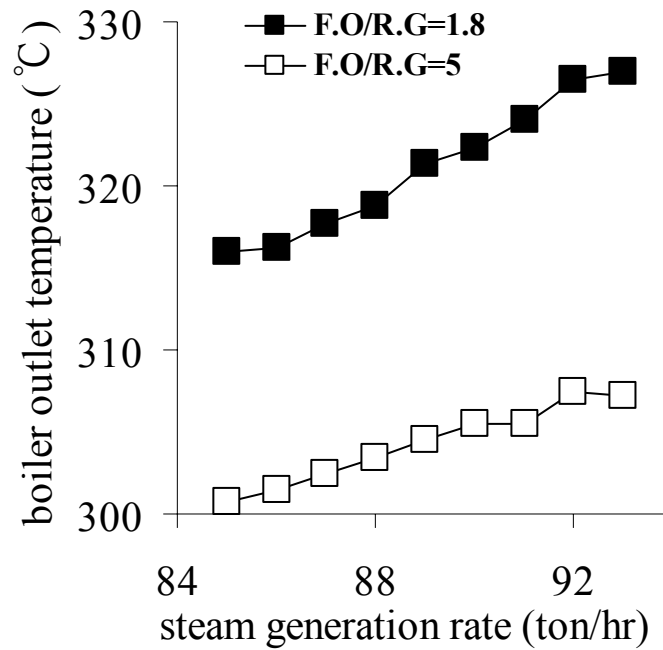


Fig. 4. Relationship between the steam generation rate and boiler outlet temperature.

By Eq. (1) and Eq. (2) (Reed, 1983), the flue-gas volume yielded out of both fuel gas and fuel oil under complete combustion was calculated as $5.945 \text{ m}^3 \text{ flue gas/m}^3 \text{ fuel gas}$ and $7.634 \text{ m}^3 \text{ flue gas/kg fuel oil}$, respectively.

Fig. 5 shows that at the FO/RG volumetric ratio of 5:1, the average flue-gas velocity was 14.45 m/s; while at rate of 1.8:1, the average was 12.75 m/s.

Higher H_2 content leads to lower concentration of carbon in the flame. Eq. (1) shows that the volume of flue gas yielded will be reduced. At the FO/RG volumetric flow rate of 5:1 more FO was used and the carbon concentration in the flame was higher; therefore, more flue gas was yielded and the flow velocity in the flue was faster.

Gaseous Fuels:

$$A_o = 1/0.21(0.5\text{H}_2 + 0.5\text{CO} + 2\text{CH}_4 + 3\text{C}_2\text{H}_4 + 3.5\text{C}_2\text{H}_6 + 5\text{C}_3\text{H}_8 + 6.5\text{C}_4\text{H}_{10} - \text{O}_2) \quad (3)$$

Liquid Fuels:

$$A_o = 8.89\text{C} + 26.7(\text{H}-\text{O}/8) + 3.33\text{S} \quad (4)$$

where

A_o : the theoretical air

By applying Eq. (3) and Eq. (4), the results are as follows:

The theoretical air volume (Nm^3) required in every 1 Nm^3 of fuel gas is calculated as $A_o=5.2$ (Nm^3), and the theoretical air volume (Nm^3/kg) in every 1 kg of fuel oil is $A_o=10.98 \text{ Nm}^3/\text{kg}$.

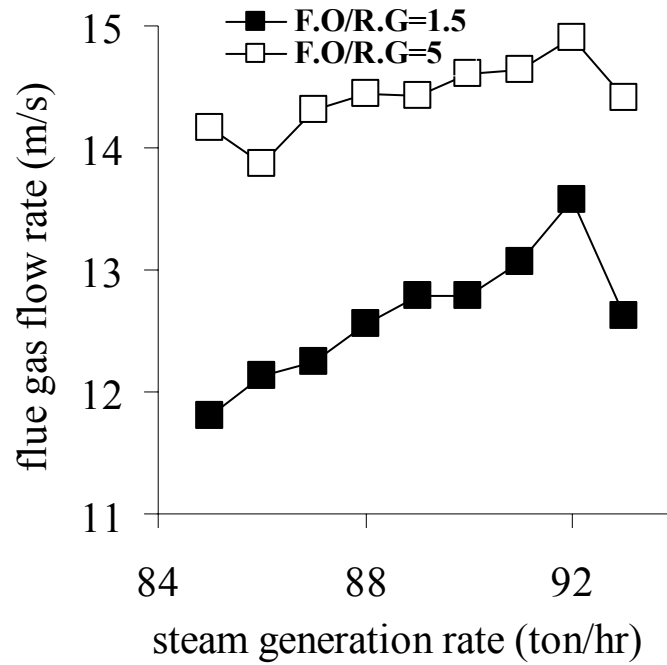


Fig. 5. Relationship between the steam generation rate and flue gas flow rate.

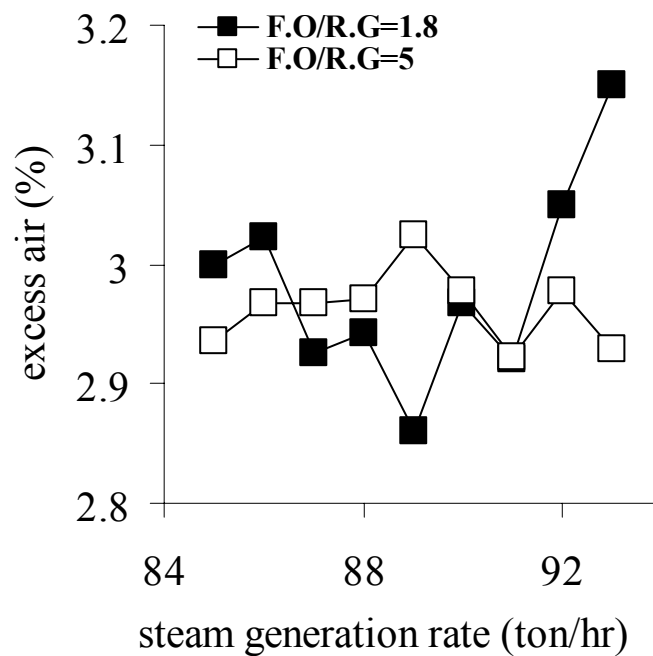


Fig. 6. Relationship between the steam generation rate and excess air (%).

Fig. 6 shows that a more theoretical air volume was required at the FO/RG volumetric flow rate of 5:1 due to higher fuel-oil consumption. Therefore, under the same steam-generating load, the O₂ concentration in the excess air was lower. Besides, the fuel oil contained a high quantity of carbon, yielding a higher volume of carbon monoxide.

Fig. 6 also shows that the volume of excess air under the FO/RG volumetric flow rate of 1.8:1 was lower than at 5:1. This was due to the fact that the fuel gas applied in the study came from the refining gas of the process, which had an H₂ content that varied from 20% to 90%. Therefore, more air would be required due to the rapid change of the H₂ content in the fuel gas and thus resulting in the decrease of the O₂ concentration in the excess air.

Economic Advantages

We analyzed the economic advantages of adjusting the FO/RG volumetric flowrate ratio from 5:1 to 1.8:1, and the results are as follows:

The average NO concentration was 167 ppm at the FO/RG ratio of 5:1 and the annual NO emission was 362 tons; while at the FO/RG volumetric ratio of 1.8:1 the average NO concentration was 152 ppm and the NO emission was 290 tons per year. Therefore, by adjusting the FO/RG volumetric flow rate from 5:1 to 1.8:1, NO emission was reduced up to 72 tons.

The average velocity of flue gas was 14.45 m/s at the FO/RG ratio of 5:1 and the air pollution fee charged by Taiwan EPS was \$4.4 million NT each year (~\$133,000 US). On the other hand, the average velocity of flue gas was 12.75 m/s at the FO/RG volumetric flow rate of 1.8:1, and the air pollution fee each year was \$3.5 million NT (~\$106,000 US). By changing the FO/RG ratio from 5:1 to 1.8:1, the annual air pollution fee was lowered by as much as \$890,000 NT (~\$27 thousand US). In addition, both the volume of carbon monoxide and O₂ in the excess air also reduced.

The fuel gas, which is a waste product of refining process, would have been expelled to the waste-gas combustion tower for burning; using more of this gas not only lowers the cost, but also reduces the volume of refining air sent to the combustion tower. Furthermore, in regard to recycling efficiency, needless to say, it also reduces NO yield in the atmosphere and meets environmental protection regulations. Furthermore, fuel costs at the FO/RG volumetric flow rate ratio of 5:1 were \$325 million NT per year (~\$11 million US); while at the FO/RG ratio of 1.8:1 the fuel cost was \$292 million NT (~\$9.1 million US). By adjusting the FO/RG volumetric flow rate ratio from 5:1 to 1.8:1, up to \$33 million NT of fuel cost was saved each year, which is more than \$1.1 million US.

There are four boilers of the same type installed in this full-scale plant; thus by adjusting the FO/RG volumetric flow rate ratio, substantially higher economic advantages are likely than shown by the test's results.

CONCLUSIONS

A study of reducing NO emission by using different FO/RG ratios in a 130 ton/hr full-scale medium-pressure steam boiler was carried out. The goal of this study was to build up an energy-saving system that would also lower the NO emission in highly efficient and environmentally friendly operational conditions. By adjusting the FO/RG volumetric flow-rate ratio from 5:1 to 1.8:1: the concentration of NO emission was reduced by 15 ppm (from 167 to 152 ppm), down 8.5%; up to \$33 million NT (~\$1.1 million US) of fuel cost was saved each year; and the average velocity of flue gas went down from 14.45 m/s to 12.75 m/s. As a result, the annual air pollution fee was down by \$890,000 NT/\$27,000 US. With a lower volume of excess air, the flow rate of gas in the furnace chamber decreased. The flow rate of heat energy ascending from the furnace-chamber radiation zone to the convection zone also slowed down. Applying refining fuel gas in the process not only lowered the NO yield, but also reduced the amount of refining gas to be burned in the waste-gas combustion tower, and thus increased the recycling efficiency.

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