Development of Extremely Low-Emission Multi-Fuel Boiler System with Plasma-Chemical Hybrid Exhaust Aftertreatment

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1 Abstract:

A plant of low emission hot water or steam supplying system which consists of a multi-fuel boiler (gas or oil fuel) and a plasma-chemical hybrid NO_x aftertreatment is demonstrated. The plant can provide renewable energy or carbon neutrality because it can use waste oil or bio-oil. The boiler has a steam generation rate of 2.5 t/h, and the flue gas flow rate is from 650 to 2150 Nm^3/h. In city gas combustion, untreated NO_x at boiler outlet of approximately 26 ppm is reduced to less than 1 ppm at the outlet of the removal apparatus during a 450 min operation. Bio-oils can be burned without problem and NO_x emission of less than 20 ppm is continuously achieved from 110-120 ppm at boiler outlet. The CO_2 reduction when heavy oil is replaced with bio-oil, is estimated. Furthermore, the system continuous operation is successfully conducted in accordance with the designated operation conditions for industrial application.

2 Introduction

Several studies have been conducted on laboratory-scale nonthermal plasma-chemical hybrid processes for the removal of NO_x from gases emitted from various stationary sources such as boilers, diesel power generators and refuse incinerators. These processes can now successfully remove almost all traces of NO_x with negligible amounts of byproducts [1]–[3]. However, because the flue gases must be treated directly, treatment of large volumes requires both a large plasma reactor and a large amount of power. An alternative process has been developed that involves the injection of ozone (O_3) or radicals generated from oxygen (O_2), ammonia (NH_3), nitrogen (N_2) and methane (CH_4) by using plasma (indirect plasma method). This process has been studied in laboratory-scale and pilot-scale

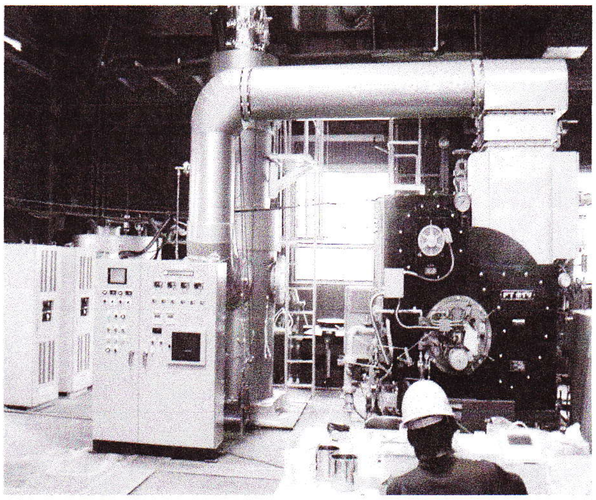

Fig. 3-1: Overview of the demonstration plant

experiments [4]–[5], where it has been found to be extremely effective for NO_x removal. This is because only the necessary amounts of gas—e.g., ambient air, O_2, NH_3, CH_4 and N_2—are treated externally at ambient temperature and pressure. The authors propose the plasma-chemical hybrid process consists of the indirect nonthermal plasma process followed by the wet-chemical treatment. The principle of the NOx reduction is as follows:

$$O_3 \rightarrow O_2 + O \quad (1)$$

$$NO + O \rightarrow NO_2 \quad (2)$$

(NO oxidation by plasma ozonizer)

$$2NO_2 + 4Na_2SO_3 \rightarrow N_2 + 4Na_2SO_4 \quad (3)$$

(by wet-chemical scrubber)

On the basis of the laboratory-scale experimental studies, tests on the removal of both NO_x and SO_x from the gas emitted from a boiler were carried out using the first pilot-scale apparatus employing the indirect

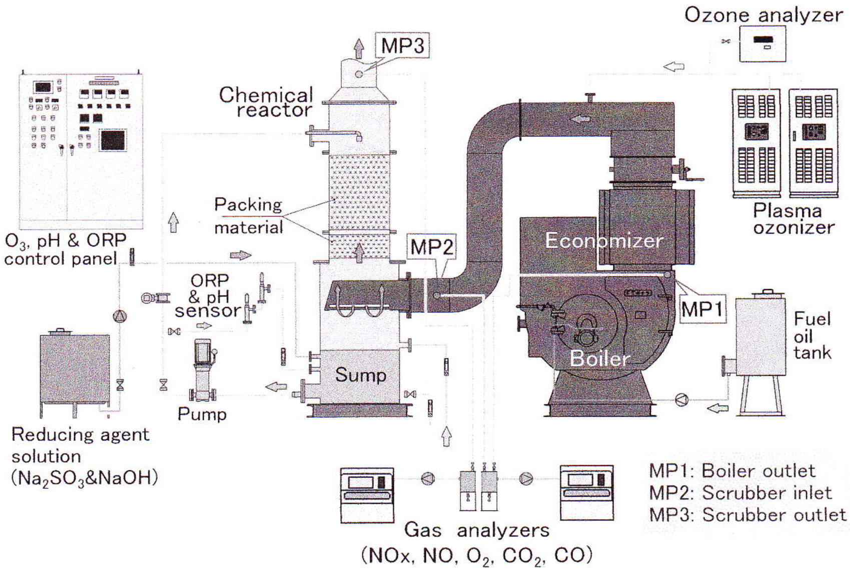

Fig. 3-2: Schematic diagram of the plant

plasma-chemical hybrid process. The NO_x removal efficiency during the combustion of compressed natural gas (CNG) exceeded 90% [6]. The further experiments were carried out using the second pilot-scale apparatus consisted of an ozonizer that was more compact and economical than the original pulsed corona reactor and a chemical scrubber that had approximately one-third the volume of the original. Continuous operation for 3–5 h was successful, and the NO_x removal performance characteristics were investigated. The amount of NO_x removed was clearly dependent on the oxidation reduction potential (ORP) of the scrubbing solution, and it increased with a decrease in the ORP. The influence of the packing material height in the scrubber on NO_x removal performance characteristics was investigated [7]–[9]. Furthermore the experiment was conducted using the third demonstration plant consisted of a multi-fuel boiler and an improved chemical scrubber. The purpose of this study was three items: the first was to decrease NO_x emission as low as possible when firing CNG, and the second was to confirm combustion characteristics and NO_x removal performance when firing bio-oils, such as WVO, rice bran oil (RBO), and fish oil. The third was to confirm the boiler system continuous operation with the NO_x removal.

3 Experimental set-up

Fig. 3-1 shows an overview of the demonstration plant. Fig. 3-2 shows a schematic diagram of the plant. The boiler (Takao Iron Co., Ltd.) had both an original burner and a low NO_x burner for gas or/and oil and was operated by using CNG (13 A) at 157 Nm^3/h, heavy oil (Type A) at 171 L/h and bio-oils. The boiler had a steam generation rate of 2.5 t/h. An economizer (exhaust gas heat exchanger) was used to recover the heat energy from the flue gas and sufficiently reduce the temperature of the flue gas to less than 150°C at the scrubber inlet to protect the polypropylene packing materials piled in the scrubber. One or two sets of commercial ozonizers (Ebara Jitsugyo Co., Ltd., EW-90Z) with a pressure swing adsorption (PSA) oxygen generator were employed for generation as described in Table 3-1; when the O_3 gas flow rate was 0.9 Nm^3/h and the discharge power was 1.5 kW, 90 g/h of ozone was generated, and its concentration was approximately 4.7%. The ozone was injected into a flue gas duct for NO oxidation. The flue gas was then introduced

Table 3-1: Specifications of plasma ozonizer

Type	Unit	EW-90Z
O_2 supply		PSA
Ozonizer type		Silent discharge
O_3 mass rate	g/h	0-90
O_3 conc.	g/Nm^3	0-100
O_3 flow rate	Nm^3/h	0.9
Power	kW	1.6(PSA) 1.5(Discharge)
Dimension	m	0.7W, 0.92D, 1.8H

Table 3-2: Oil fuel properties

Item	unit	Heavy oil	WVO	RBO	Fish oil
Calorific value	J/kg	44940	37560	36260	37740
Dynamic viscosity	mm^2/s (40°C)	5~10	39.2	17.9	26.2
Flash point	°C	60	298	192	184
Residual carbon	%	0.06	0.37	0.11	0.83
Nitrogen	%	0.01	0.01	<0.05	0.21
Sulfer	%	0.059	<0.01	<0.01	<0.01

into the scrubber with a height of 3.7 m to reduce NO_2. The diameters were 0.9 m at the sump part of the scrubber and 0.7 m at the packing material layer part. The scrubbing solution was pumped from the sump to the top of the scrubber and sprayed through a nozzle over the packing material of which the height was set to 1.2 m. After the NO_x in the flue gas was removed in the scrubber, the cleaned flue gas was discharged in the air through the smokestack. On the other hand, the scrubbing solution passed through the packing layer into the sump was circulated by a multistage centrifugal pump operating at 1.5 kW. A small amount of scrubbing solution was continuously drained from the scrubber to keep the activity of the solution, i.e., remove the reaction product from the scrubber solution. The liquid flow rate was set to 3.0 m^3/h by controlling the valve at the outlet of the circulating pump. Meters installed on a tributary line connected to the sump monitored the ORP and pH of the scrubbing solution. An aqueous solution of Na_2SO_3 and NaOH (concentrations: 200 g/L and 10 g/L) obtained from a chemical factory as a byproduct was continuously added into the sump. The flow rate of the fresh aqueous solution was carefully controlled according to the pH and ORP of the scrubbing solution. The initial Na_2SO_3 concentration of the scrubbing solution in the sump was set to more than 16 g/L. Experiments were performed after the temperature of the flue gas reached a steady state. The boiler was operated at 30%–100% of the boiler rated load. The flow rate of the flue gas was determined by a practical formula based on the fuel flow rate and O_2 concentration of the flue gas at the boiler outlet.

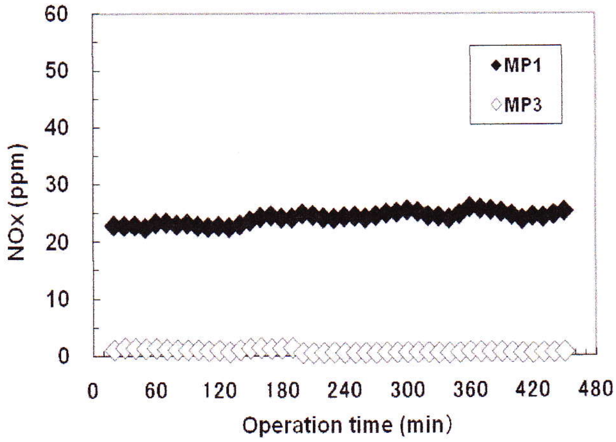

Fig. 4-1: NO_x (5% O_2 converted value) at MP1 and MP3 vs. operation time when firing CNG

The flue gas temperature was measured using thermocouples. The concentrations of the flue gas constituents (O_2, CO_2, CO, NO_x and NO) were measured by using gas analyzers (Horiba PG-240). The temperature of the flue gas and concentrations of its constituents were measured at the following three sampling points (Fig. 3-2): MP1 (boiler outlet), MP2 (scrubber inlet) and MP3 (scrubber outlet). The O_3 concentration generated by the ozonizer was measured by using an O_3 monitor (Ebara Jitsugyo Co., Ltd., EG-550). The experiments were carried out by firing CNG, and heavy oil and bio-oils. Table 3-2 shows the fuel properties of both heavy oil and bio-oils. The experiment was carried out for 120–450 min on a single day.

4 Experimental results and discussion

NO_x emitted from a boiler can be reduced by means of boiler combustion improvement, such as low NO_x burner, exhaust gas recirculation, and steam or water injection, etc. Two kinds of burner were applied, an original burner and a low NO_x burner developed in this study. The relationship betwen NO_x concentrations and flue gas fow rate at MP1 was investigated. When firing CNG, flow rates of the flue gas ranged from 650 to 2150 Nm^3/h. O_2 concentration of flue gas was in the range of 3.8-4.9%. Here the NO_x concentrations were described as the converted value at 5% O_2 concentration by rule in the case of gasous fuel (hererafter NO_x is described as the O_2 converted value). The NO_x concentrations were within 45-49 ppm at any gas flow rate using the original burner. On the other hand the NO_x concentrations were also within 23-26 ppm

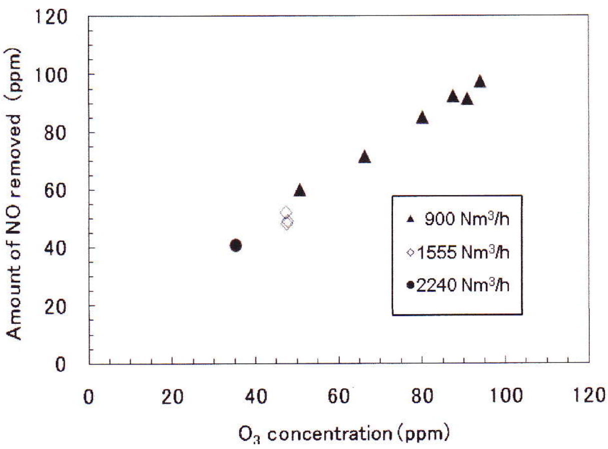

Fig. 4-2: Relation between the amount of NO (4% O_2 converted) removed and the O_3 concentration in the duct when firing heavy oil

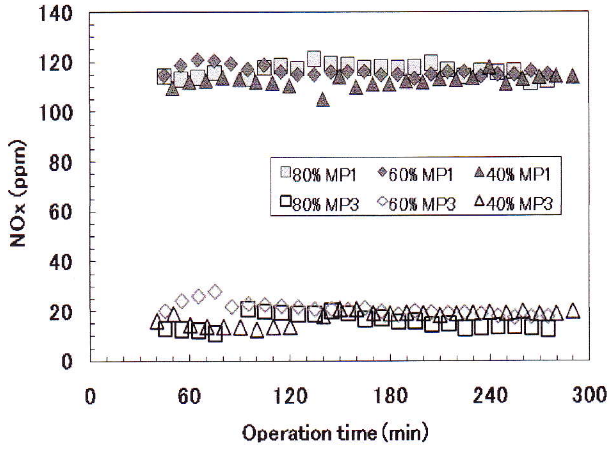

Fig. 4-3: NO_x (4% O_2 converted) at MP1 and MP3 vs. operation time when firing WVO mixed oil

when using the low NO_x burner. It is clear that NO_x concentrations were reduced to approximately 50% at any gas flow rate by means of the low NO_x burner. This NO_x reduction was much more than expected. The experiment was proceeded using the low NO_x burner in order to investigate NO_x emission at MP3 as low as possible. Fig. 4-1 shows the time-depended NO_x at MP1 and MP3 during a 450-min operation period when firing CNG. CNG of 52 Nm^3/h was combusted with O_2 concentration of 4.6%, and the flow rate of the flue gas was 756 Nm^3/h at MP1. O_3 was injected at rate of 43 g/h and the average injection rate of Na_2SO_3 solution was 5.6 kg/h. The result was that the NO_x concentrations at MP1 were within 22-25 ppm, and the NO_x concentration at MP3 was quite low, less than 1 ppm throughout the experiment. The NO_x removal efficency was more than 96.6 % on average. This proved that the target of extreme low NO_x emission could be nearly acheived when firing CNG.

After the CNG combustion tests, heavy oil or/and bio-oil combustion tests were carried out to measure the flue gas constituents and NO_x removal performance. The effect of ozone injected into the flue gas on the amount of NO was confirmed. Fig. 4-2 shows the relationship between the amount of NO removed from the flue gas and the ozone concentartion estimated in the flue gas duct where O_3 was injected. Flow rates of the flue gas were set to 900, 1555, and 2240 Nm^3/h, respectively, when firing heavy oil. The O_3 concentrations were from 35 ppm up to 100 ppm. It is clear that the amount of NO removed was nearly the same as the amount of the corresponding O_3 concentration in order to oxidize NO to NO_2 (1:1 stoichiometric ratio) regardless of the flue gas flow rate. Mixed oil tests of bio-oil and heavy oil were conducted. Firstly, WVO was mixed with heavy oil. The mixed oils were made up of 40%, 60%, and 80% WVO corresponding to 60%, 40%, and 20% (vol.) heavy oil, respectively (hereafter called 40-80% WVO mixed oil). Fig. 4-3 shows the time depended NO_x concentrations at MP1 and MP3 for 40%, 60%, and 80% WVO mixed oils. The flow rates of the flue gas were 920, 977, and 990 Nm^3/h, respectively. O_3 was injected at rate of 146-151 g/h and the average injection rate of Na_2SO_3 solution was 12.6-14.3 kg/h. The NO_x concentrations at MP1 increased a little by 10 ppm from 102 ppm, 110pm, and 107ppm for 40%, 60%, and 80% WVO mixed oils, respectively as time went on. The NO_x concentrations at MP3 fluctuated within 150-min, but became stable, approximately 20 ppm for all cases. The NO_x removal efficencies were 82.4-86.5% on average. it proved that the WVO mixed oil could be combusted satisfactorily up to 80% mixture ratio.

Secondarily, RBO was mixed with heavy oil. The mixture ratios of RBO to heavy oil were set to 20%, 30%, and 50% (vol.) in a stepwise fashon. The RBO mixed oils were combusted at rate of 66-67 L/h with O_2 concentration of 6.4-6.9% and CO_2 of 10.7-10.2%. The CO concentrations were less than 3 ppm for the all cases. The flow rate of the flue gas was 947-962 Nm^3/h at MP1. The rates of O_3 injected were 132-147 g/h and the average injection rate of Na_2SO_3 solution were 11.0-12.6 kg/h. Fig. 4-4 shows the time depended NO_x concentrations at MP1 and MP3 for 20%, 30%, and 50% RBO mixed oils during 120-240 min operation periods. The NO_x concentrations at MP1 were quite stable and almost unchanged, 109-112 ppm on average. The NO_x concentrations at MP3 were almost stable, less than 20 ppm for all cases. The NO_x removal efficencies were 82.3-88.7%. The oil BRO mixed oil could be combusted up to 50%

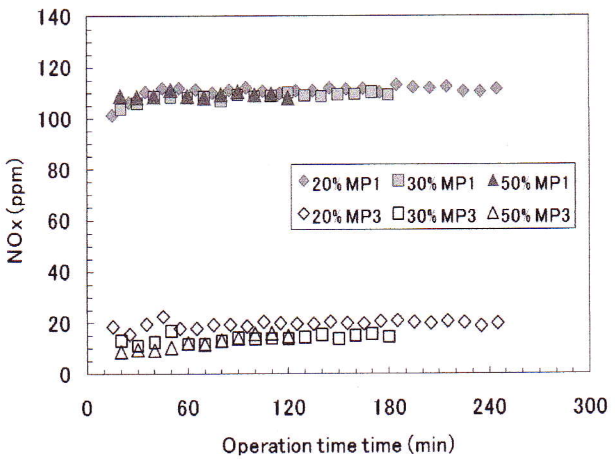

Fig. 4-4: NO_x (4% O_2 converted) at MP1 and MP3 vs. operation time when firing RBO mixed oil

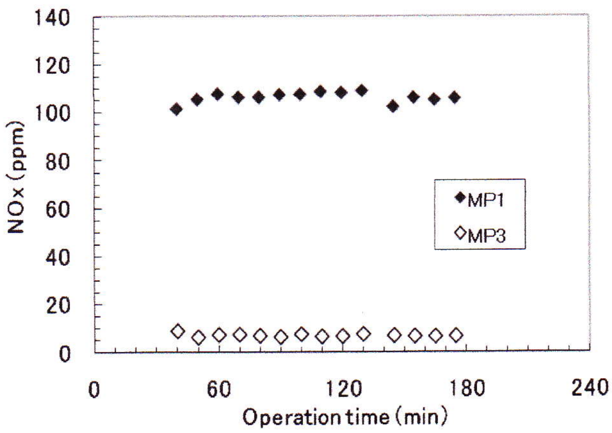

Fig. 4-5: NO_x (4% O_2 converted) at MP1 and MP3 vs. operation time when firing fish mixed oil

mixture ratio without problem. For reference it is careful to handle RBO because RBO got hard due to high viscosity in case of low ambient temperature. RBO must be preheated higher than 40°C in the storage tank.

Thirdly, fish oil was combusted without heavy oil. Fish oil was combusted at rate of 68 L/h with O_2 concentration of 4.2% and CO_2 of 12.6%. The CO concentration was approximately 2 ppm. The flow rate of the flue gas was 857 Nm^3/h at MP1. The rate of O_3 injected was 148 g/h and the average injection rate of Na_2SO_3 solution was 12.9 kg/h. Fig. 4-5 shows the time depended NO_x concentrations at MP1 and MP3 during a 180-min operation period. The NO_x concentrations at MP1 were stable, 106 ppm and the NO_x concentrations at MP3 were quite stable, less than 7 ppm througout the experiment. The NO_x removal efficencies were 93.2% on average. Fish oil could be solely combusted without problem.

Bio-fuel is carbon neutral and is acknowledged to have less CO_2 emissions than other fuel types. When heavy oil (fuel rate: 171 L/h) was burned at the rated value of the boiler, the concentration of CO_2 was calculated to be 11.6% in the flue gas, and the total amount of CO_2 emitted from the boiler was estimated to be 3700 t/year for 8000 h operation in a year. Therefore, if 80% WVO mixed oil (20% heavy oil) is burned, CO_2 emission is reduced yearly by 80% to 2960 t.

For industrial application of the multi-fuel boiler system, it is essential to confirm the proper operation of the system which consists of a boiler and a NO_x removal apparatus. The aim of the system operation was to confirm that NO_x removal apparatus can be properly operated in accordance with the boiler operation conditions. If the fuel flow rate changes, the rate of steam generation changes. The steam generation is dependent on the steam demand for the customer at the designated steam pressure in boiler operation as well. Furthermore, if the fuel flow rate changes, the flow rate of the flue gas changes. On the other hand the injection rates of O_3 and Na_2SO_3 are main factors for NO_x removal performance. Those correlates closely with the flow rate of the flue gas, that is to say with the fuel flow rate of boiler. The system continuous operation was conducted when firing CNG. The three fuel flow rates were set to 70, 111, and 137 Nm^3/h, respectively and changed by the automatic control every 30-min after 60-min from the plant start. The flow rate of the flue gas were 1065, 1685, and 1945 Nm^3/h, respectively during a 360-min operation period. Fig. 4-6 shows the time depended steam generation rate and the pressure of the boiler. In result the steam pressure was within 0.35-0.4 MPa as nearly same as the desiginated value and the steam could be produced at the desiginated generation rate. Fig. 4-7 shows the time dependded NO_x concentrations at MP1 and MP3 during the system continuous operation. The NO_x concentrations at MP1 were within 22-25 ppm, almost no difference in spite of the change of the fuel flow rate. The NO_x concentrations at MP3 were less than 5 ppm throughout the experiment. The NO_x removal efficencies were 92.5-80.9%. The NO_x removal performance could keep well by controlling the proper injection rates of O_3 and Na_2SO_3 depending on the fuel flow rate. It proved that the system continuous operation was successfully conducted in accordance with the designated operation conditions.

5 Conclusion

Extremely low-emission multi-fuel boiler system with plasma-chemical hybrid exhaust

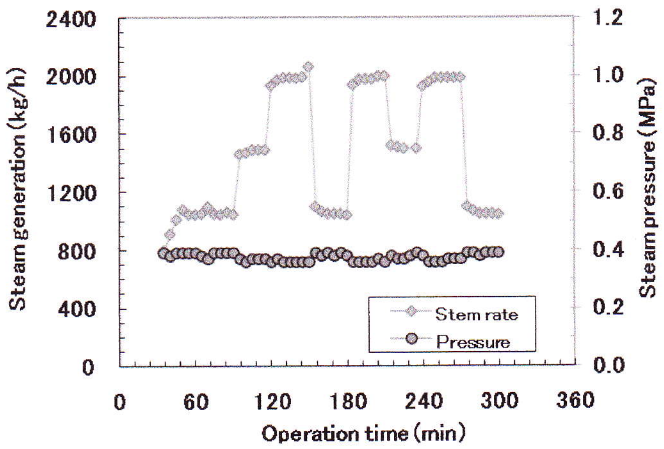

Fig. 4-6: Steam generation rate and pressure vs. operation time when firing CNG

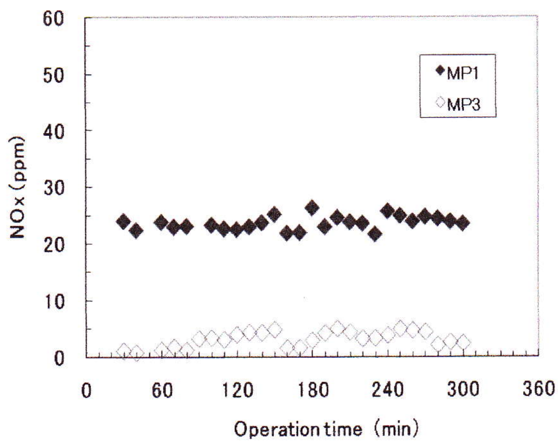

Fig. 4-7: NO_x (5% O_2 converted) at MP1 and MP3 vs. operation time when firing CNG

aftertreatment was examined. The followings are concluded.

The NO_x concentrations at MP1 (boiler outlet) while firing CNG could be reduced to approximately 50%, from 45-49 ppm to 23-26 at any gas flow rate by means of the low NO_x burner developed in this study. Futhermore, the NO_x concentration at MP3 (scrubber outlet) was quite low, less than 1 ppm during a 450-min operation period. This proved that the target of extremely low NO_x emission could be nearly acheived when firing CNG.

Secondarily when firing bio-fuels, those were investigated the combustion characteristics of muti-fuel boiler and the NO_x removal performance. In result regarding the combustion characteristics, 30-80% WVO, 20-50% BRO mixed oils, and 100% fish oil could be burned without probelm. Flue gas constituents were very similar to those of heavy oil. The NO_x concentrations at MP1 were 110-120 ppm, by 10-20 ppm more than that of heavy oil. The NO_x concentrations at MP3 were less than 20 ppm for all cases, which were satisfacory emission. The effect of replacing heavy oil with bio-oil can reduce CO_2 emissions from the boiler because bio-fuel is carbon neutral. If 80% mixed oil (20% heavy oil) is burned, the amount of CO_2 discharged into the air is reduced by 80% to 2960 t for an 8000-h operation in a year.

Thirdly, for industrial application of the multi-fuel boiler system, it is essencial to confirm the proper operation of the system which consists of a boiler and a NO_x removal apparatus. The system operation was conducted when firing CNG. The fuel flow rate was set to 45-87% of the boiler rated load by the automatic control every 30-min. The steam rate and the steam pressure could be produced at the desiginated values. The NO_x removal performance could keep well by controlling the proper injection rates of O_3 and Na_2SO_3 depending on the fuel flow rate. It proved that the system operation was successfully conducted in accordance with the designated operation conditions.

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