Prediction Methodology of Fuel-NOx Emissions in Gasified Fuels' Combustion

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ABSTRACT

Gasification technologies enable conversion of low-grade resources to clean gases, and can generate electricity through gas turbine. However, gasified fuels contain nitrogenous compounds of NH_3 and HCN that cannot be removed in the case of employing a hot/dry-type synthetic gas cleanup for improvement of plant thermal efficiency and are oxidized into fuel-NOx in combustion processes. Fuel-NOx emissions constitute the majority of NOx emissions in exhaust. In combustion processes of the CO, H_2 and CH_4 mixture fuels, the oxidation characteristics of nitrogenous compounds are different from cases of conventional hydrocarbon fuels, and influenced by fuel constituents and combustion methods. Author had clarified influence of gasified fuel constituents on fuel-NOx emissions through experiment. This paper clarifies that conversion rate of nitrogenous compounds to fuel-NOx is decided by both a CH_4 concentration and primary equivalence ratio in the case of using two-stage combustion, while conversion rate is greatly affected by an H_2 constituent in the case of gasified fuel containing no CH_4. Consequently, a prediction methodology of conversion rate of fuel-N is established in the case of air-staging two-stage combustion.

INTRODUCTION

Our lives rely heavily on energy, or mostly the fossil fuels that lead to carbon dioxide emissions in modern society. In the intervening quarter-century, the amount of electricity generation in the Asia/Oceania region increased about four times, while world electricity generation doubled (Official Energy Statistics from the U.S. Government, World Electricity Data, 2006). Conventional thermal electricity generation covers 78 percent of the demand increase in Asia/Oceania, with both hydroelectricity and nuclear power generation at about 11 percent respectively. Our lives are currently linked to the amount and availability of fossil fuels (Hasegawa, 2007a). From the viewpoints of securing a stable supply of energy and protecting our global environment into the future, it is obvious that we must seek to find new ways to make highly effective use of waste matter as a recyclable energy resource as well as unused resources in low-rank coal, tar crude, oil shale, and biomass.

Transportation and chemical products needs liquid fuels such as crude oil, the electricity generation industries consume natural gas, coal and nuclear power as well as that oil. In addition to high-efficiency use of existing fossil energy, researches for promoting advanced uses of nonfossil energies have been done worldwide. For example, biomass and waste are positioned as environmentally-friendly and renewable sources of energy, which are scattered across the globe, or thinly distributed. We have to develop technologies to convert each source into high quality energy, such as liquefaction and gasification technologies.

In this paper, author will pick out the gasification technology as one of these technologies and discuss the combustion characteristics of various gasified fuels derived from all kinds of gasification processes and feedstock. Gasification technologies that have been investigated worldwide since the 1970s enable conversion of low-grade, hardly used resources including coal, pet coke, oil residues, waste and biomass to clean gases, and can generate electric power through advanced technologies in highly-efficient gas turbine combined cycle power generation. In the cases of gaseous fuels that consist of CO, H_2 and CH_4, such as gasified fuels and blast furnace gases, there is a possibility of containing a small amount of nitrogenous compounds in the form of NH_3 mostly. In the case of employing the hot/dry synthetic gas cleanup (Nakayama et al, 1990) to improve the plant thermal efficiency, the NH_3 cannot be removed and is oxidized into fuel-NOx in the combustion processes. The fuel-NOx constitutes the majority of NOx emissions in the exhaust. Development of combustion technology to reduce fuel-NOx emissions is the crucial issue. From the consideration about experimental data obtained ever in greater details through reaction kinetics analyses, author will clarify inhibition mechanisms of fuel-NOx and basic principle of prediction methodology of the conversion rate of fuel-bound nitrogenous compounds to fuel-NOx. The technical findings would enable to predict NOx emissions using various gasified fuels and contribute to development of the improved low-NOx combustor.

NOMENCLATURE

CO/H_2 : molar ratio of carbon monoxide to hydrogen in fuel
CO : carbon monoxide emissions in exhaust ppm
C.R. : conversion rate from ammonia to NOx %
HHV : higher heating value at 273K, 0.1MPa basis MJ/m^3
LHV : lower heating value at 273K, 0.1MPa basis MJ/m^3
NOx : nitrogen oxide emissions in exhaust ppm
T_{air} : temperature of supplied air K
T_{ex} : average temperature of combustor exhaust gas K
T_{fuel} : temperature of supplied fuel K
V_{fuel} : fuel injection velocity m/s
ϕ_{ex} : average equivalence ratio in entire combustor
ϕ_p : average equivalence ratio in primary combustion zone

BACKGROUND

Table 1 (Ashizawa et al., 1996),(Bush et al., 1991),(Consonni et al., 1997),(Cook et al., 1994),(Hasegawa, 2006a and 2006b), (Ichikawa and Araki, 1996),(Kalsall et al., 1994),(Smith, ed., 1993),

(Smith, ed., 1994), (Ueda et al., 1995) shows the typical compositions of fossil-based gasified fuels, and three types of gases: blast furnace gas (BFG), coke-oven gas (COG) and converter gas (Linzer donawitz gas: LDG) produced in iron works. Similarly, table 2 shows examples of various gasified fuels using nonfossil resources such as various types of wood (Moritsuka, 2007), solid municipal waste, refuse-derived fuel (RDF) and black liquor. Each gaseous fuel contains CO and H_2 as main combustible components, and small amounts of CH_4. Trace constituents of nitrogenous compounds and sulfur are heavily dependent upon upgrade or cleanup processes for gasified fuels. The nonfossil energies of thinly-distributed biomass and waste is expected to provide CO_2-free energy of local production for local consumption. Since upgrade and cleanup processes must be simplified to improve the nonfossil-base gasification power plant, those gasified fuels contain tar and dust. Fuel calorific values vary widely (2-13MJ/m^3 of HHV basis), from about one-twentieth to one-third those of natural gas, depending upon the raw material of feedstock, the gasification agent and the gasifier type. For one thing, gaseous fuels derived from solid municipal waste and water-coal slurry by

gasification contain high concentrations of steam. In recent cases of by-product gaseous fuels in iron works, LDG produced at intervals, but which has three times the heat capacity as BFG is also going to be used for power generation. It is therefore necessary to adopt suitable combustion technologies for each gaseous fuel.

With regard to fossil-based gasification technology, commercially-based power plants have been developed with new development challenges being addressed toward global carbon capture storage (Isles, 2007). Meanwhile, in response to the oil crisis of the 1970s, development of biomass-fueled gasification received considerable attention worldwide. For example, in northern Europe, fixed-bed gasification heating plants built in the 1980s had been in commercial operation. The available technical and economical operation data convinced small district heating companies that biomass or peat-fueled gasification heating plants in the size class of 5MW were the most profitable (Haavisto, 1996). In the United States, kraft recovery process based upon indirectly heated black liquor gasification technology had been developed (Kelleher, 1985). In the stable period of oil prices and the global economy, however, nonfossil-fueled gasification had not received

Table 1 Typical compositions of derived gases from fossil-base gasifiers and furnaces

Fuel	BFG[a]	COG[b]	LDG[c]	Gasified fuel									
Resource				Coal[d]								Heavy residue	Orimulsion[TM]
Coal type or mine				1	-[g]	2	3	4	5	6	7		
Gasifier type				Fixed	Fluidized			Entrained				Entrained	Entrained
Coal supply				Dry	Dry			Dry			Slurry		
Developer				BGL	BC	IGC		Shell		HYCOL	Texaco	Texaco	CRIEPI
Oxidizer				O_2	Air	Air		O_2		O_2	O_2	O_2	O_2
Composition													
CO [%]	20	6	75	56.4	7.9-14.7	27.6	25.9	67.8	69.5	55.2-59.4	40.9	51.7	43.5
H_2 [%]	3	56	-[f]	25.6	13.2-15.0	9.4	10.9	28.8	31.0	31.1-33.7	29.9	43.1	42.2
CH_4 [%]	-[f]	30	-[g]	6.6	1.5- 2.8	0.5	1.4	0.01	0.03	1.0- 2.0	0.1	0.2	0.4
CO_2 [%]	20	-[f]	13	2.8	10.0-12.0	5.4	6.7	2.3	1.0	7.6-10.4	9.5	3.2	11.8
H_2O [%]	-[f]	-[f]	-[g]	-[g]	11.5-18.4	-[g]	-[g]	-[i]	-[i]	-[g]	12.3	-[i]	-[i]
NH_3 [ppm]	-[f]	-[f]	-[g]	-[g]	500-1000	1000[h]		100	600	-[g]	-[g]	-[g]	-[g]
H_2S+COS[ppm]	-[f]	-[f]	-[g]	20	-[g]	714	404	1.1%	0.14%	-[g]	-[g]	1.6%	1.35%
Others[%]	N_2	C_2H_2 etc.	O_2,N_2	8.6	45.9- 47.3	56.1	54.2	-[g]	-[g]	-[g]	7.3	0.2	0.75
CO/H_2 mole ratio	7	0.1	-[f]	2.2	-[g]	2.9	2.4	2.1	2.4	1.6-1.9[h]	1.4	1.2	1.0
HHV[MJ/m^3]	2.9	21[h]	9.5[h]	13.0	-[g]	4.9	5.2	12.2	12.5	12.0[h]	9.0	12.1[i]	11.0[i]
LHV [MJ/m^3]	2.9	19[h]	9.5[h]	12.0	3.6- 4.1	3.6	3.9	11.7	11.9	11.3[h]	7.4	11.3[i]	10.2[i]

[a] BFG: Blast furnace gas, [b] COG: Coke-oven gas, [c] LDG: Converter gas
[d] 1=High-sulphur bituminous coal, 2=Moura coal, 3=Taiheiyo coal, 4=Illinois No.5 coal, 5=Sufco mine, 6=Taiheiyo coal, 7=Moura coal,
[f] Unknown, [g] No description, [h] Estimated values, [i] Dry Base

Table 2 Typical compositions of gasified fuels from nonfossil resources

Resource	Wood																Waste[k]	RDF[m]	Black Liquor
Feedstock type	Planer chip		Mill ends			Planer Bark briquette		Waste chip	Pellet		Round timber chip			Chip					
Moisture content[%]	13.3		45	27	15	8	9	-[g]	-[g]		-[g]		-[g]	15 – 40			-[f]	-[f]	-[g]
Gasifier type	Kiln		Fixed-bed down-draft						Fluidized										Entrained
Developer	Chugairo Co.Ltd.		Kawasaki Heavy Ind.					Indian Inst. Sci.	Lurgi		Guessing		CHOREN Ind.	Tampella					Chemrec
Oxidizer	dry distillation	$+O_2$	Air					Air	Air	O_2	Air+steam	Air	O_2	Air+steam			Air	Air+O_2	O_2
Composition																			
CO [%]	36.1	26.0	9.7	14.6	20.6	19.8	17.9	19	20	46	25	22	40	8.0-15.0			6	30	38.08
H_2 [%]	20.2	30.1	11.2	14.3	16.7	15.2	14.5	16	10	13	40	22	40	8.0-12.0			1.6	22	39.17
CH_4 [%]	16.6	2.5	1.2	1.4	1.3	1.9	1.3	12	5	10	10	-[g]	-[g]	4.0- 8.0			0.9	0.4	1.34
CO_2 [%]	15.8	17.9	-[g]	-[g]	-[g]	-[g]	-[g]	2	14	23	22	11	20	13.0-18.0			12.4	4.1	19.05
H_2O [%]	-[g]	-[g]	1.3	0.7	2.8	0.9	1.8	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	7.0-15.0			23.4	5.9	0.18
N_2 [%]	5.6	17.9	56.9	53.5	50.2	49.9	52.1	51	51	8	-[g]	45	-[g]	-[g]			-[f]	-[f]	0.24
NH_3 [ppm]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]			-[g]	-[g]	-[g]
H_2S+COS[ppm]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]			-[f]	-[f]	19400
Others[%]	5.7	5.6	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]			N_2, C_2H_4etc.	N_2	-[g]
Tar [mg/m^3]	25000	5	261	438	95	400	103	100	-[g]	-[g]	-[g]	-[n]	-[n]	-[g]			-[f]	-[f]	115
Dust[mg/m^3]	11000	< 2	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	< 5			-[f]	-[f]	-[g]
CO/H_2 mole ratio	1.8	0.9	0.9	1.0	1.2	1.2	1.2	1.2	2	3.5	0.6	1.0	1.0	-[g]			3.8	1.4	1.0
HHV[MJ/m^3]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]	-[g]			1.8	6.8	10.3
LHV [MJ/m^3]	15.2	7.5	3.1	4.0	5.0	5.1	4.5	5.4	6.3	11.7	13.8	6.3	10.5	4 - 6			1.2	6.2	9.5

[f] Unknown, [g] No description, [k] Municipal solid waste, [m] RDF: Refuse derived fuel, [n] Undetected

considerable interest. Then in the early 2000s when the Third Conference of Parties to the United Nations Framework Convention on Climate Change (COP3), invoked mandatory carbon dioxide emissions reductions on countries, biomass-fueled gasification technology began to receive considerable attention as one alternative.

Author has engaged in researches on the combustion reaction characteristics of various gasified fuels and gas turbine combustors. As part of the research in nitrogenous compound's behavior in the gasified fueled combustions, effects of the methane constituent on optimization of the two-stage combustion to reduce fuel-NOx emissions could be clarified (Hasegawa et al, 2001). Author thinks over those phenomena from a theoretical standpoint and then, reaches a conclusion of relationship between fuel-nitrogenous compound's behavior and fuel constituents on the basis of the research findings.

Based on the previously published findings, this paper describes the behavior of fuel nitrogenous compound in non staging diffusion combustion and two-stage combustion, and the prediction methodology of the nitrogenous compounds conversion to fuel-NOx. Its knowledge would present engineering guidelines of the combustor designs for various gasified fuels.

EXPERIMENTAL DEVICE AND METHODS

Experimental Device

Figure 1 gives an outline of the basic experimental device (Hasegawa et al., 2001). Combustion air is controlled to the required amount by an orifice meter and flow control valve, heated to the prescribed temperature by an electric heater, and then blown into the combustor. Primary air is injected into the combustor through a primary air swirler positioned around the fuel injection nozzle, and secondary air is supplied through air holes in the sidewalls of the combustor.

CO and H_2, which are the main combustible components of the fuel, are mixed in the prescribed blend ratios and loaded into a cylinder to be used. The combustible components are diluted with N_2 to adjust the required calorific value, heated to the prescribed temperature by an electric heater, and fed through the fuel injection nozzle. The small amounts of NH_3 and CH_4 are controlled by each thermal mass flow controller, and premixed with the fuel before reaching the fuel injection nozzle. In the case of adding CH_4, the fuel calorific value is adjusted depending on the amount of the N_2 dilution while maintaining the CO/H_2 molar ratio constant.

Exhaust gases are sampled from the exit of the combustor through a water-cooled stainless steel probe and continuously introduced into an emission console that measure CO and CO_2 by infrared analysis, NOx by chemiluminescence analysis, O_2 by paramagnetic analysis, and hydrocarbons by flame ionization. The sampling probe is located at a distance of about 1.5m downstream from the burner. Concentrations of calibration gases for CO, CO_2, O_2, NO, and CH_4 are 270ppm, 18%, 20%, 20ppm for low-range of NO and 180ppm for high-range NO, and 90ppm respectively. Each repeatability of the analyzer is between –0.5 and +0.5 % of full-scale range, linearity is between –1.0 and +1.0 % of full-scale range or between –2.0 and +2.0 % of measure readings, and noise is less than 1.0% of full-scale range.

Figure 2 shows a vertical sectional view of the combustor and tested diffusion burner (Hasegawa et al., 2001). The combustion apparatus consists of a cylinder-style combustion chamber with an inner diameter, D, of 90mm and a length of 1000mm, and a primary air swirler and fuel injection nozzle. The combustion chamber is lined with heat insulating material and the casing is cooled with water. There are four sections for secondary-air inlets on the sidewall of the combustion chamber along the direction of flow to simulate a two-stage combustion or secondary air of the combustor. Secondary air inlets are used at a distance from the edge of the fuel injection nozzles of $3 \times D$. The diameter of the secondary air inlets at the entry to the combustion chamber is 13mm, and six inlets are

positioned on the perimeter of one cross-section. The tested burner consists of a fuel injection nozzle and a primary air swirler. There are twelve injection inlets with a diameter of 1.5mm on the fuel injection nozzle with an injection angle, θ, of 90-degrees. The primary air swirler has an inner diameter of 24.0mm, an outer diameter of 36.4mm, and twelve vanes with a swirl angle, θ_a, of 45-degrees. Swirl number, S, which is calculated from the following equation, is 0.84.

$$S = \frac{2}{3} \times \frac{1-B^3}{1-B^2} \times \tan\theta_a \quad \text{..} \quad (1)$$

Where B (boss ratio of swirl vane) = 0.66.

Supplied Fuels and Test Conditions

Table 3 shows the typical supplied fuels and test conditions. In the tests, fuel calorific values are varied between 2.9 and 12.7MJ/m³, the CO/H_2 molar ratios in the fuels are set to values of 0.43, 1.00 and 2.33, and the small quantity of CH_4 in the fuels is varied to investigate the typical combustion characteristics of the gaseous fuels produced from various gasification systems. Temperatures of supplied fuel and air, and fuel injection velocity are set at constant for each combustion test. All of combustion tests are conducted under atmospheric pressure conditions. Based on the experiments and analyses, the fuel-NOx emission characteristics are examined in non staging combustion and two-stage combustion.
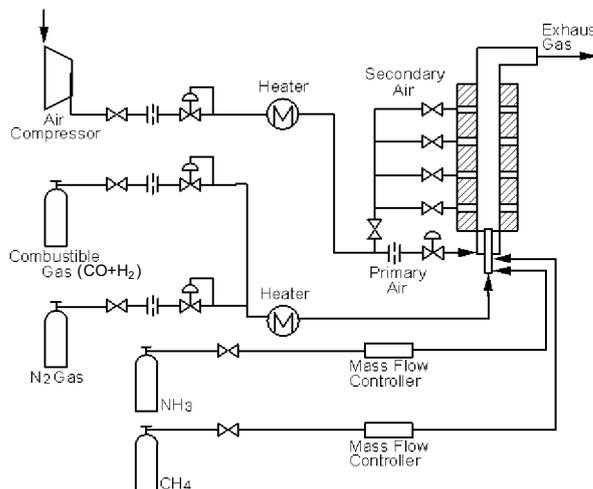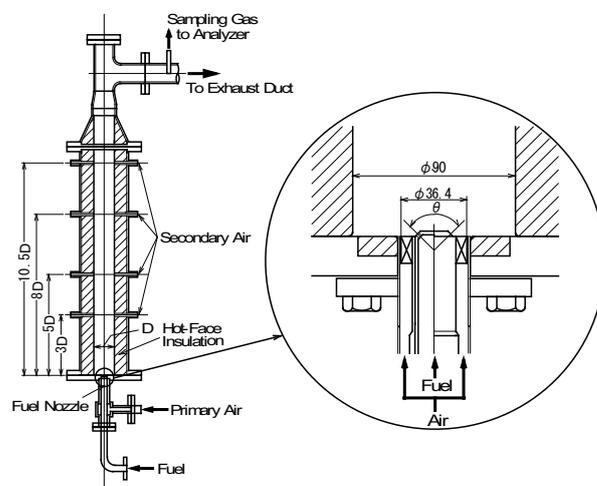

Fig.1 Schematic diagram of basic experimental device

D : inner diameter of cylinder-style combustion chamber, 90mm
θ : injection angle of fuel nozzle, 90 degrees

Fig.2 Sectional view of combustion chamber and diffusion burner

NOx EMISSION CHARACTERISTICS

Effects of Reducing Combustion

There have been a huge number of researches about the combustion characteristics of gasified fuels (Morgan and Kane, 1962), (Coward and Jones, 1971), (Yamagishi et al., 1974), (Martin and Dederick, 1977), (Ishibasi et al., 1978), (Folsom et al., 1980), (Ishizuka and Tsuji, 1981), (White et al., 1983), (Drake et al., 1984), (Döbbeling et al., 1996), (Zanello and Tasselli, 1996) and combustors (Pillsbury et al., 1976), (Battista and Farrell, 1979), (Clark et al., 1982), (Beebe et al., 1982), (Döbbeling et al., 1994), (Cook et al., 1994). Earlier studies by author et al. (for example, 1998a, 1999, 2001, 2003, 2005, 2007b) have suggested advantages of the reducing combustion to reduce both fuel-NOx emissions and thermal-NOx emissions in gasified fueled combustion through experiments and analyses. Unlike the case of a hydrocarbon flames, however, the prompt NO could be produced little in the cases of gasified fuels because gasified fuels have a small percent of methane. Zel'dovich NO is very low compared with fuel-NOx emissions in the case of low-Btu gasified fuels because of the low flame temperature of low-Btu fuel. On the other hand, calorific values of gasified fuels differ according to both gasification systems and feedstock, or the maximum flame temperatures of the oxygen-blown gasified, medium-Btu fuels are raised and thermal-NOx emissions increase. Since abovementioned examination involves the main message of this paper deeply, I would like to refer the combustion characteristics concerned.

Figure 3 shows the relationship between the equivalence ratio, ϕ_{ex}, and both the conversion rate of NH_3 in the fuel to NOx, C.R., and NOx emission concentrations, when a fuel higher heating value is set to 4.4 MJ/m^3 (at 273K, 0.1MPa), and when 1000ppm of NH_3 and no CH_4 are included in the fuel (Hasegawa et al., 2001). All combustion air is provided from the primary air swirler that surrounds the fuel injection nozzle. During the test, the temperature of the combustion air, T_{air}, is preset and maintained at 673K and the temperature of the fuel, T_{fuel}, at 423K. The equivalence ratio is adjusted by controlling the flow of combustion air while maintaining a constant fuel flow. The fuel injection velocity, V_{fuel}, is set and maintained at 92m/s. The conversion rates of NH_3 in the fuel to NOx are calculated from the measured values of the thermal-NOx and the total NOx emissions. The concentration of thermal-NOx, $[NOx_{th}]$, is first measured after stopping the supply
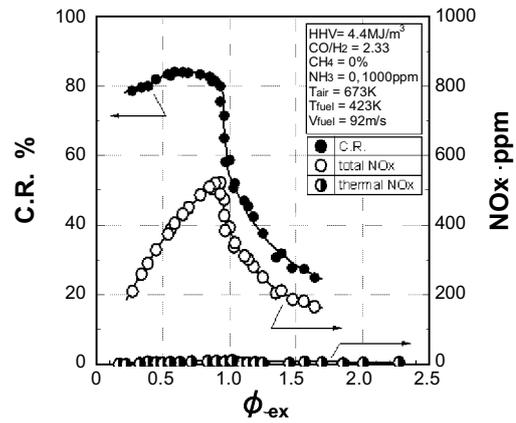

Fig.3 NOx emissions characteristics in low-Btu fueled combustion (Hasegawa et al., 2001)

of NH_3, and the concentration of total NOx, $[NOx]$, is measured while NH_3 is supplied. Then finally, fuel-NOx is calculated by deducting the concentration of thermal-NOx from that of total NOx. The conversion rates are given by the following equation:

$$C.R. = \frac{([NOx]-[NOx_{th}]) \times (\text{volume flow rate of exhaust})}{[NH_3] \times (\text{volume flow rate of fuel})} \quad \cdots (2)$$

As shown in figure 3, the conversion rates of NH_3 in the fuel to NOx indicated a value higher than 80% when the equivalence ratio was less than 1.0 of stoichiometric conditions (i.e., fuel-lean condition). When the equivalence ratio exceeded 1.0 (i.e., fuel-rich condition), the conversion rate rapidly dropped. Figure 3 also shows thermal-NOx emissions, but its value is very low because the low-Btu fuel of around $4MJ/m^3$ is lower maximum flame temperature of around 2000K. Meanwhile, in the cases of CO and H_2 mixture, medium-Btu fuels of $8MJ/m^3$ or higher, the maximum flame temperatures are higher than that of methane and thermal-NOx is emitted in large amounts (Hasegawa et al., 2001). The reducing combustion could also reduce thermal-NOx emissions as well as fuel-NOx emissions in cases of the medium-Btu fuels (Hasegawa et al., 1997). From the above-mentioned results, it is clarified that the fuel-NOx and thermal-NOx emission characteristics in reducing combustion are different from those in non-reducing combustion of the gasified fuels of CO and H_2 mixtures. Therefore, the predictions of fuel-NOx emissions both in non-staging, non-reducing combustion and two stage combustion are examined in the followings.

Effects of Fuel H_2 Constituent in Non Reducing Combustion

The gasified fuels vary in constituents as shown in table 1 and table 2. Figure 4 shows influence of the CO/H_2 molar ratio in the fuel on relationships between equivalence ratio, ϕ_{ex}, and the conversion rate of NH_3 in the fuel to NOx, C.R., (Hasegawa et al., 2001). The test conditions are the same as the case of figure 3, except for changing the CO/H_2 molar ratio in the fuels. The fuel calorific values are adjusted by N_2 dilution. When the equivalence ratio was less than 1.0, the conversion rates of NH_3 to NOx were almost constant and those values increased in proportion to the CO/H_2 molar ratio. However, when the equivalence ratio is more than 1.0, significant impact of CO/H_2 molar ratio on the conversion rate is not observed.

As described above, the influence of the CO/H_2 molar ratio on the fuel-NOx emissions show different tendencies between the cases of fuel-lean combustion conditions and fuel-rich, reducing combustion. Author therefore investigated the influence of CO/H_2 molar ratio on fuel-NOx emission characteristics in the cases of diffusion flames of fuel-lean conditions, before examining effects of the two-staged reducing combustion on fuel-NOx emissions.

Figure 5 shows the relationship between the fuel calorific value and the conversion rate of NH_3 to NOx with the CO/H_2 molar ratio

Table 3 Standard test conditions

Fuel properties / Conditions	Fuel No.					
	1	2	3	4	5	6
Constituent CO [vol%]	Standard conditions					
	24.3	17.3	10.4	23.1	16~70	23.1~12.1
H_2 [vol%]	10.4	17.3	24.2	9.9	7~30	9.9~5.2
CH_4[vol%]	0, (2.6[*1])			0	0	0~5.0[*1]
NH_3[ppm]	0, 1000					
N_2 [vol%]	Balance[*3]					
CO/H_2 molar ratio	2.33	1.00	0.43	2.33	2.33 (1, 0.43)[*2]	2.33
HHV[MJ/m^3] (at 273K, 0.1MPa)	4.4			4.2	2.9~12.7	4.2
LHV[MJ/m^3] (at 273K, 0.1MPa)	4.2	4.1	3.9	4.0	2.8~12.1	4.0~3.9
T_{fuel} [K]	298			633		503
T_{air} [K]	673			643		503
V_{fuel} [m/s]	32, 92			96		
Pressure	Atmospheric pressure condition					

*1: In the case of varying CH_4 concentration in the fuel, the CO and H_2 constituents were adjusted to maintain the fuel calorific value and the CO/H_2 molar ratio constantly.

*2: The cases of the CO/H_2 molar ratios of 1.00 and 0.43 were investigated as well as 2.33.

*3: The fuel calorific values were adjusted by N_2 dilution.

as a parameter (Hasegawa et al., 1997). Each fuel contains 1000ppm NH_3 and no CH_4, the average exhaust gas temperature, T_{ex}, is set and maintained at a 1773K constant. In the case of changing fuel calorie, the calorific value and the equivalence ratio are adjusted by N_2 dilution and by airflow rate, respectively, maintaining the CO/H_2 molar ratio in the fuel at each constant value of 0.43, 1.00 and 2.33. During the tests, all combustion air is provided from the primary air swirler around the fuel injection nozzle, and all fuel is from that fuel injection nozzle. Temperature of the combustion air, T_{air}, is preset and maintained at 643K and the temperature of the fuel, T_{fuel}, at 633K. The fuel injection velocity, V_{fuel}, is set and maintained at a 96m/s constant by controlling the N_2 dilution and supply of CO and H_2 constituents. The equivalence ratio is adjusted by the flow rate of combustion air to make T_{ex} at 1773K constant while maintaining a constant fuel volume flow.

In each case of the fuel CO/H_2 molar ratio, the conversion rate of NH_3 to NOx indicated a similar tendency with the rise in fuel calorific value: in the lower fuel calorie range, the conversion rate rose rapidly with the rise in fuel calorie except in the case of a CO/H_2 molar ratio of 0.43, and showed each local maximal value. When the fuel calorie increased further, conversion rates decreased and indicated local minimal values; and then those conversion rates rose slightly with fuel calorie increases.

It is generally accepted that a decrease in the dilution with inert gases, or an increase in the concentration of nitrogenous compounds suppresses the conversion rate of nitrogenous compounds into NOx (Fenimore, 1972), (Sarofim et al., 1975), (Kato et al., 1976), (Takagi et al., 1977). In the case of figure 5, the NH_3 concentration is constant, but the ratio of NH_3 to combustible components, $NH_3/(CO+H_2)$, decreases with a decrease in N_2 dilution. In the case of the phenomena in figure 5, however, three overall reactions appeared in a multilayered way against the foregoing research results. After an exhaustive study of the above phenomena through analyses based on full kinetics, it was clear that the behavior of nitrogenous compounds in the CO and H_2 mixture fuels were greatly affected by an H_2 constituent. As a result, the author has reorganized the data in figure 5 to observe the effects of an H_2 constituent on fuel-N conversion.

In figure 6, the horizontal axis indicates H_2 concentration in each fuel, or variances in fuel calorie with respect to each fuel CO/H_2 molar ratio while maintaining an average T_{ex} constant. In the range where the CO/H_2 molar ratio is between 0.43 and 2.33, the conversion rates of NH_3 to NOx vary depending on H_2 concentration without relying on CO concentration, fuel calorific value and equivalence ratio: The conversion rate is inversely proportional to H_2 concentration in a range between 10% and 30% of H_2. And when H_2 concentration increases to 30% or higher, the conversion rate increases in slight proportion to the H_2 concentration.

That is, it is said that similar findings with the results of Fenimore (1972) are observed in lower concentrations of H_2 in the case of CO and H_2 mixture fuel, and with the conversion rate of NH_3 to NOx inversely proportional to H_2 concentration in the range of H_2 30% or lower. However, the reverse tendency takes place under conditions where H_2 concentration is 30% or higher: where the decrease in the amount of N_2 dilution, or the increase in the H_2 concentration raises the conversion rate slightly without relying on a CO constituent.

The conversion rate of the fuel-N compounds to NOx greatly depends on the ratio of fuel-N compounds to the combustible component of H_2 under conditions where the amount of fuel-N compounds is constant. Except in the case of higher concentrations of CO with nominal amounts of N_2 dilution, the conversion rate is decided only by the H_2 concentration at any CO/H_2 molar ratio. In the case of a diffusion flame, both the oxidation reaction rate and preferential diffusion of H_2 are faster than those of CO, and radicals such as OH and O are produced early. That is to say, the conversion rate is greatly affected by the H_2 concentration without relying on a CO constituent. This, however, does not necessarily mean that a CO

constituent makes no dent in the conversion rate. When the CO concentration in the fuel increases more than five out of ten times, the influence of a CO constituent becomes relatively higher. The higher the CO/H_2 molar ratio, the more the conversion rate shows an overall trend to increase on a same footing as H_2 concentration.

Moreover, under conditions of higher H_2 concentration in the fuel, the countertrend of the examination by Fenimore (1972) takes place, or a decrease in the amount of N_2 dilution increases H_2 concentration in the fuel and slightly raises the conversion rate of fuel-N compounds to NOx.

Furthermore, in the case of fuel including the lower combustible components, the maximum flame temperature becomes low, but a
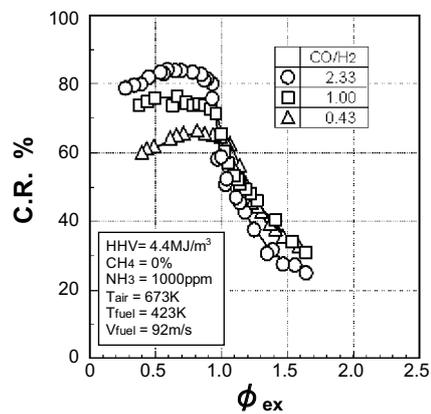

Fig.4 Effects of CO/H_2 molar ratio on conversion rate of NH_3 in fuel to NOx (Hasegawa et al., 2001)
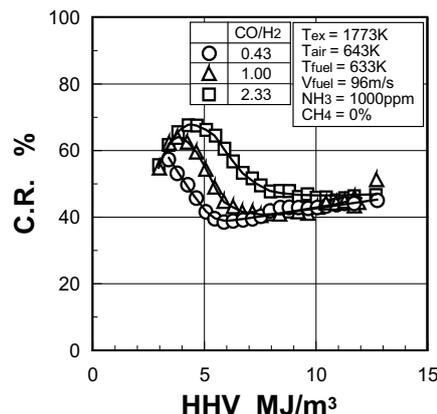

Fig.5 Effects of gasified fuel calorie on conversion rate of NH_3 to NOx in each case of fuel including no methane (Hasegawa et al., 1997)
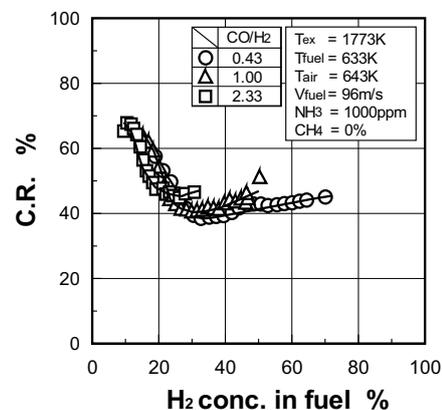

Fig.6 Effects of H_2 constituent in fuel on conversion rate of NH_3 to NOx. Data in figure 5 was rearranged.

small amount of H_2 constituent contributes to the production of OH and O radicals in flame and lowers the temperature of selective reduction of fuel-N to N_2 in the presence of an O_2 constituent, as shown by following overall reaction. The conversion rate is strongly

$$NH_3 + NO + 1/4O_2 \Leftrightarrow N_2 + 3/2H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots(3)$$
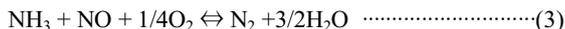
affected by the H_2 constituent and decreases with a rise in H_2 concentration under conditions of lower H_2 concentration in the fuel. But a large amount of H_2 constituent in the fuel should suppress the decomposition of fuel-N compounds and delay the reduction reaction of fuel-N to N_2. Consequently, the intermediates obtained by decomposition of the fuel-N are exposed to an atmosphere of higher O_2 concentration, and the conversion rate increases reversely. From the above reasons, the conversion rates of fuel-N compounds in a fuel rarefied environment indicate the behaviors shown in figure 6.

NOx EMISSION CHARACTERISTICS IN SUPPLIED-AIR STAGING COMBUSTION

Two-stage combustion with reducing flame, which has a primary stage combustion under a fuel-rich condition and a secondary stage where the remaining unburned fuel combusts completely, is widely accepted as combustion technology to suppress the fuel-NOx production in conventional fuels (Martin and Dederick, 1977), (Yamagishi et al., 1974), (Pratt et al., 1971). It is also known that the fuel-NOx production mechanisms of conventional hydrocarbon fuels such as CH_4 are different from that of non-hydrocarbon fuels such as CO and H_2 (Fenimore, 1976), (Heap et al., 1976), (Takagi et al., 1978), (Kato et al., 1977). Because the non-hydrocarbon fuels hardly produce the species of HCN. Gasified fuels consist of CO and H_2 as main combustible components, but also contain between thousands of ppm and a small percent of CH_4.

In the preceding section, it became clear that the effects of H_2 on the fuel-NOx production in the conventional diffusion combustion of CO and H_2 mixture fuels, as shown in figure 6. On the other hand, when adopting the reducing flame of two-stage combustion to reduce the fuel-NOx production, author et al. have clarified the followings (Hasegawa et al., 2001): In order to adopt the two-stage combustion to the CO, H_2 and CH_4 mixture fuels effectively, it is necessary to make the reducing condition of the first-stage combustion appropriate depending on the fuel constituents, because the intermediate of HCN is produced in the fuel-rich and lower temperature conditions; and the influences of the CO/H_2 molar ratio in the fuels on the appropriate condition of primary-stage are different between the fuel including CH_4 and the fuel including no CH_4, as shown in figure 7; in the case of fuel including CH_4, the appropriate condition of primary-stage vary depending on the CH_4 concentration in the fuel, as shown in figure 8.

In the following sections, author indicates the combustion test results of figure 7 and 8, and reviews the influencing factors of fuel constituent and the equivalence ratio in the primary-stage combustion zone on the fuel-NOx reduction. In accordance with the results of a series of considerations, the prediction methodology of fuel-NOx emissions would be clarified from engineering viewpoint.

Effects of Fuel Constituents

Effect of CO/H_2 molar ratio in fuel. Figure 7 shows the correlation between the primary equivalence ratio, ϕ_p, in two-stage combustion and the conversion rate of NH_3 in the fuel to NOx using the CO/H_2 molar ratio as a parameter, under conditions where the average equivalence ratio at the combustor exit, ϕ_{ex}, is set to 0.44 for each case of fuel containing 2.6% of CH_4 and fuel containing no CH_4 (Hasegawa et al., 2001). In each case, the fuel calorific value is maintained at 4.4MJ/m^3 and the NH_3 concentration is 1000ppm. When the fuel contained no CH_4, the fuel CO/H_2 molar ratio wielded a significant effect on the conversion rate of NH_3 to NOx

under conditions where the primary equivalence ratio was less than 1.0, or both the primary and the secondary zones had excess air combustion. When the primary equivalence ratio was 0.44, the conversion rate was 47% in the case where the fuel CO/H_2 molar ratio was 0.41, while the conversion rate was 68% in the case of a CO/H_2 molar ratio of 2.33. It meant that the conversion rate tended to increase proportionally to the CO/H_2 molar ratio. The difference in the conversion rates between the cases where the CO/H_2 molar ratios were 0.41 and 2.33 was about a constant 20% under conditions where the primary equivalence ratio was within the range of less than 1.0. When the primary equivalence ratio was over 1.0, the difference in the conversion rates decreased with the rise in the primary equivalence ratio. Those conversion rates then approached each other and showed equal values when the primary equivalence ratio was 2.5. However, when the fuel contained 2.6% CH_4, a significant impact of CO/H_2 molar ratio on the conversion rate was not observed under test conditions where the primary equivalence ratio was between 0.44 and 2.2.

The reason why significant effects could be expected of the CO/H_2 molar ratio in the case of a diffusion flame of fuel containing no CH_4 was that CO was oxidized more slowly in the flame front than the case of H_2, and so the higher the CO/H_2 molar ratio, the slower the O_2 consumption rate in the flame sheet. Consequently, NH_3 was oxidized under conditions of higher O_2 concentration and the NOx production rate increased, as shown in figure 7. This was, however, different from the non staging combustion. The conversion rate of NH_3 to NOx was slightly affected by the CO/H_2 molar ratio even when the primary equivalence ratio exceeded 1.0. This is because a small portion of
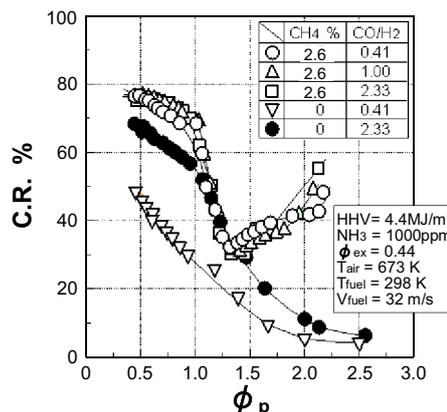

Fig.7 Influence of CO/H_2 molar ratio and CH_4 concentration on conversion rate of NH_3 to NOx in two-stage combustion (Hasegawa et al., 2001)
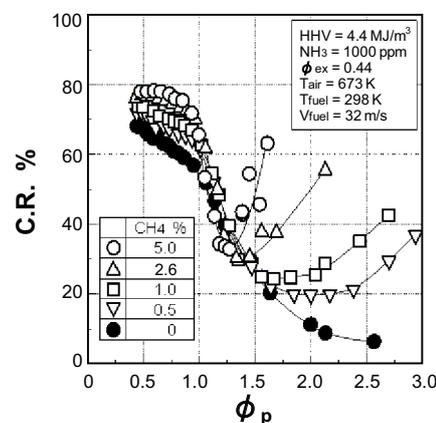

Fig.8 Influence of CH_4 concentration on conversion rate of NH_3 to NOx in two-stage combustion (Hasegawa et al., 2001)

secondary-air flowed backwards into the primary-combustion zone and slightly decreased the primary equivalence ratio, and reactions of the intermediate products produced in the primary, fuel-rich combustion zone progressed in actuality by the small portions of the secondary-air supplied into the primary zone. On the other hand, with fuel containing CH_4, the CO/H_2 molar ratio did not wield a significant effect on the fuel-NOx emission characteristics. This is because intermediates $CH_{i (i=0,1,2,3)}$ produced in the oxidation process of CH_4 affected the decomposition of NH_3, rapidly producing HCN and $NH_{i(i=0, 1, 2)}$, etc. in the flame zone, which quickly oxidized to NOx in the secondary combustion zone.

From the abovementioned results, it was clear that the relationships between the primary equivalence ratios and the conversion rates of fuel-N compounds in CO, H_2 and CH_4 mixture-fueled, two-stage combustion were greatly affected by a CH_4 constituent. Next, the effects of a CH_4 constituent will be discussed in detail.

Effect of CH_4 concentration in fuel. Figure 8 shows the correlation between the primary equivalence ratio, ϕ_p, in two-stage combustion and the conversion rate of NH_3 in fuel to NOx, C.R., with CH_4 concentration as a parameter, under conditions where the fuel calorific value is set to 4.4MJ/m^3, the NH_3 concentration in the fuel is 1,000ppm, and the fuel CO/H_2 molar ratio is 2.33 (Hasegawa et al., 2001). When changing the CH_4 concentration, the fuel calorific value is adjusted by N_2 dilution while maintaining the CO/H_2 molar ratio at a constant value of 2.33. In the examination range of figure 8, the measured thermal-NOx emissions were as low as 10ppm, because the maximum theoretical adiabatic flame temperature of gasified fuel with a fuel calorie of 4.4MJ/m^3 was lower than 2000K. When the primary equivalence ratio was less than 1.0, the conversion rate of NH_3 to NOx increased in direct proportion to the CH_4 concentration. And when ϕ_p was more than 1.0, or the primary combustion zone was in a fuel-rich condition, the conversion rate decreased as the primary equivalence ratio increased in the case of CH_4-free fuel. Meanwhile, fuel containing CH_4 had an appropriate primary equivalence ratio, ϕ_p^*, at which the conversion rate dropped to a minimum, and ϕ_p^* varied with the CH_4 concentration. That is, ϕ_p^* increases as the CH_4 concentration decreases. From these results, it can be concluded that an appropriate primary equivalence ratio, ϕ_p^*, must be determined depending on CH_4 concentration when applying two-stage combustion to gasified fuels containing CH_4 to suppress fuel-NOx emissions.

The influence of a CH_4 constituent on the conversion rate of fuel-N compounds in CO, H_2 and CH_4 mixture-fueled, two-stage combustion, have already been discussed by way of experiment (Hasegawa et al., 2001). I would however like to discuss the phenomena in greater detail once again from the viewpoint of reaction kinetics, and propose a basic principle for a prediction methodology regarding fuel-NOx emissions.

Analysis using elementary reaction model. The phenomena shown in figure 8 was caused by a selective reduction reaction of NH_3 in fuel with NO originating from N_2 in the atmosphere and fuel-bound nitrogen. NH_3 and NO are decomposed into N_2 under the coexistence of O_2 in the reducing conditions by the following overall reaction (3). The selective reduction between NH_3 and NO

$$NH_3 + NO + 1/4O_2 \Leftrightarrow N_2 + 3/2H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$
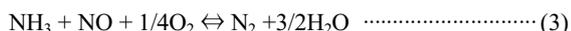
is influenced by the reaction temperature, NH_3/NO molar ratio, O_2 concentration, fuel CO/H_2 molar ratio, and fuel CH_4 concentration in the flame zone. As a result, the rate of overall reaction (3) rises steeply to maximum in a narrow temperature range, or "temperature window". The activated chemical species such as OH, O and H radicals promote the oxidation decomposition reactions of NH_3 and CH_4, and produce the intermediate products of $NH_{i (i=0,1,2)}$ and $CH_{i(i=1,2,3)}$. The HCN is produced by interactions between the

intermediates of nitrogenous compounds and those of hydrocarbons in the reducing combustion conditions as well as the abovementioned selective reduction of NH_3 with NO. In the primary, fuel-rich combustion zone, HCN production increases proportionally to the concentration of CH_4 in the fuel, and HCN is oxidized into fuel-NO with the secondary-air supply. Consequently, it is expected that reduction of NH_3 into N_2 is restrained with a rise in CH_4 concentration in the fuel, and the optimum primary-equivalence ratio, ϕ_p^*, that minimizes the conversion rate of NH_3 to NOx declines and approaches stoichiometric conditions, while the conversion rate increases.

The abovementioned phenomena are deductively examined using numerical analysis based on the following elementary reaction kinetics. The reaction model employed here was proposed by Miller and Bowman (1989), and the appropriateness of the model for non-catalytic reduction of NH_3 using NO (Hasegawa et al., 1998b) and oxidation of ammonia by premixed methane flame (Miller and Bowman, 1989) has been confirmed by comparison with experimental results. The reaction scheme is composed of 248 elementary reactions and 50 species are taken into consideration. Miller and Bowman described both a detailed scheme of the oxidation of C_1 and C_2 hydrocarbons under most not too fuel-rich conditions and an essential scheme for ammonia oxidation. Hasegawa et al. (1998b) united those two schemes and confirmed the applicable scope of a united scheme through experiments using a flow tube reactor. Various reaction schemes have been proposed worldwide for each reaction system, and those elementary reaction models and rates require sustained confirmation and revisions. For example, Glarborg et al. (1995) investigated the reaction of NH_3 with NO_2 through a flow reactor and detailed reaction kinetics, Bromly et al. (1995) examined effects of NO on oxidation of H_2, and Dagaut et al. (2003) studied effects of NO and SO_2 on oxidation of CO-H_2 mixtures. Recently, Smith, G.P. et al. have come out with brand-new schemes that need not be used because the gasified fuel contains a small percent of CH_4 and no C_2 hydrocarbon. Thermodynamic data is taken from the JANAF thermodynamics tables (Chase et al., 1985), and the values of other species not listed in the tables are calculated based on the relationship between the Gibbs' standard energy of formation ($\Delta G°$) and the chemical equilibrium constant (K).
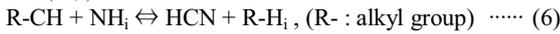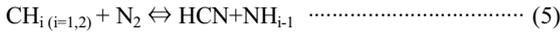
$$\Delta G° = R \cdot T \cdot ln(K) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (4)$$

In the above formula, the value of $\Delta G°$ is obtained from the CHEMKIN database (Kee et al., 1990). This study uses the GEAR method (Hindmarsh, 1974) for numerical analysis, as an implicit, multi-stage solution.

The Pratt model (1971) for flow inside the combustor simplifies flows linearly and each stage combustion zone is assumed to be a perfectly stirred reactor. Also, it is assumed that the species are evenly mixed in the reaction process, and diffusion and stirring processes are not taken into consideration. Correctly solving full reaction kinetic processes with flow processes at the same time is at present confined to a simple axisymmetric laminar jet flow (Xu et al., 1997) field with numerical analysis. In order to precisely clarify here the reaction processes in two-stage combustion, the oxidation and reduction reaction processes of fuel-N compounds are traced through full reaction kinetics analyses, while the complex flow inside the combustor is modeled on the Pratt method from a macroscopic standpoint. And the residence time in each combustion zone is calculated on the assumption that the each mixing gas temperature is regarded as the adiabatic flame temperature corresponding to each equivalence ratio.
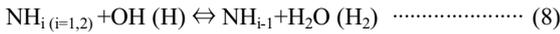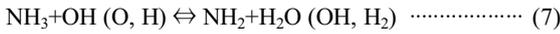
It has been widely reported that HCN is not produced in non-hydrocarbon flame even if the fuels contain nitrogenous compounds such as NH_3 (Kato et al., 1977). In the hydrocarbon flame, HCN is produced from nitrogen in the air by reaction (5), and is rapidly oxidized and produces prompt NO. With the CO, H_2 and CH_4 mixture fuels including NH_3, following the

decompositions of CH_4 and NH_3, if HCN was produced by reaction (6) in the fuel-rich region of flame, then that HCN is oxidized to NO
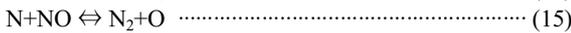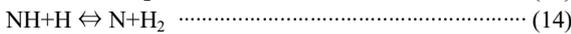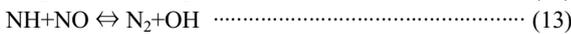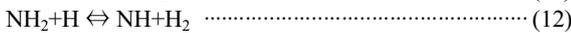
$$CH_{i(i=1,2)} + N_2 \Leftrightarrow HCN + NH_{i-1} \quad \cdots\cdots\cdots\cdots\cdots\cdots (5)$$
$$R\text{-}CH + NH_i \Leftrightarrow HCN + R\text{-}H_i \text{ , (R- : alkyl group)} \quad \cdots\cdots (6)$$
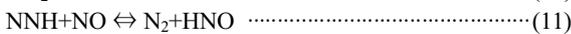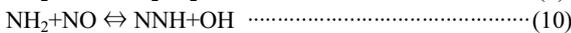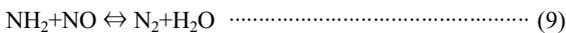
in the fuel-lean region. The nitrogen of NH_3 has weaker bonding power than in the case of N_2.

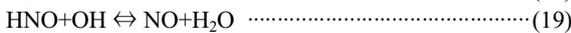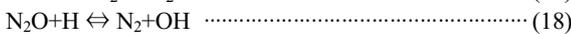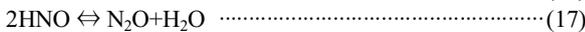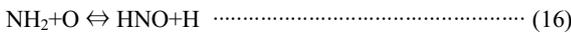In the early process of the reaction, the radical chemical species of OH, O and H are rapidly formed before the decomposition of NH_3. In the combustion process, NH_3 reacts with the OH, O and H radicals and then easily decomposes into the intermediate $NH_{i\,(i=0,1,2)}$ by the following reactions, as has been reported by Miller et al. (1983).

$$NH_3 + OH \text{ (O, H)} \Leftrightarrow NH_2 + H_2O \text{ (OH, } H_2) \quad \cdots\cdots\cdots\cdots (7)$$
$$NH_{i\,(i=1,2)} + OH \text{ (H)} \Leftrightarrow NH_{i-1} + H_2O \text{ (} H_2) \quad \cdots\cdots\cdots\cdots (8)$$
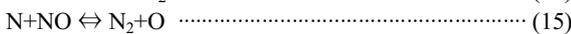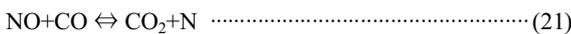
$NH_{i\,(i=0,1,2)}$ is oxidized into NO in the conventional combustion processes under ample air conditions. When hydrocarbon is not contained in the fuel, NH_i can be converted into N_2 by reacting with NO in the fuel-rich region. The overall reaction (3) is manifested as the following elementary reactions.

$$NH_2 + NO \Leftrightarrow N_2 + H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (9)$$
$$NH_2 + NO \Leftrightarrow NNH + OH \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (10)$$
$$NNH + NO \Leftrightarrow N_2 + HNO \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (11)$$
$$NH_2 + H \Leftrightarrow NH + H_2 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (12)$$
$$NH + NO \Leftrightarrow N_2 + OH \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (13)$$
$$NH + H \Leftrightarrow N + H_2 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (14)$$
$$N + NO \Leftrightarrow N_2 + O \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (15)$$

Also, part of the NH_2 produced as a product of decomposition of NH_3 is oxidized into HNO by the O radical through reaction (16). Some HNO produced by reactions (11) and (16) are decomposed into N_2 by reactions (17) and (18), and the remainder are oxidized into NO by reactions (19) and (20).

$$NH_2 + O \Leftrightarrow HNO + H \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (16)$$
$$2HNO \Leftrightarrow N_2O + H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (17)$$
$$N_2O + H \Leftrightarrow N_2 + OH \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (18)$$
$$HNO + OH \Leftrightarrow NO + H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots (19)$$
$$HNO + H \Leftrightarrow NO + H_2 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (20)$$
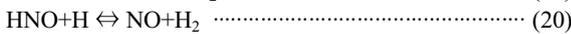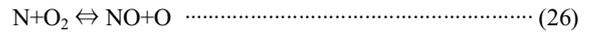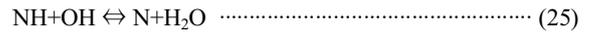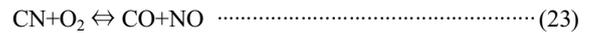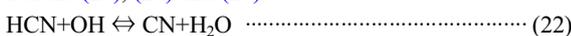
Because of the high concentration of CO in the gasified fuel, NO is reduced to an N radical with oxidization of CO to CO_2 by reaction (21), and the N radical promotes the reduction of NO into N_2 by reaction (15).

$$NO + CO \Leftrightarrow CO_2 + N \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (21)$$
$$N + NO \Leftrightarrow N_2 + O \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (15)$$

On the other hand, if fuel contains CH_4, the intermediate HCN is produced by reactions (5) and (6) in the fuel-rich primary-combustion zone. When the primary equivalence ratio is a fuel-rich condition, both the decompositions of CH_4 and NH_3, and the NO production are delayed, and HCN is produced in higher concentration. The reasons for the initiation reaction being delayed in fuel-rich conditions are due to both the lower temperature and the reductive conditions. The HCN is oxidized slowly in the primary combustion zone of the reductive atmosphere, while the HCN is rapidly decomposed into NO in the case where the primary equivalence ratio is less than 1.0 of the stoichiometric conditions. Following the decomposition of HCN, the NH_3 and CH_4 are reproduced, while at the same time, the decomposition into N_2 through those HCN and NH_3 partially progresses in the primary zone of the reductive atmosphere. Consequently, the reduction of NH_3 into N_2 is inhibited.

Some HCN is oxidized into NO by reactions (22) and (23), and the rest are decomposed into an N radical by the reaction (24) in the fuel-lean secondary zone. The NH radical is oxidized into the NO by reactions (25), (26) and (27).

$$HCN + OH \Leftrightarrow CN + H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots (22)$$

$$CN + O_2 \Leftrightarrow CO + NO \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (23)$$
$$CN + O \Leftrightarrow CO + N \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (24)$$
$$NH + OH \Leftrightarrow N + H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (25)$$
$$N + O_2 \Leftrightarrow NO + O \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (26)$$
$$N + OH \Leftrightarrow NO + H \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (27)$$

HCN production in the reducing primary combustion zone increases with rises in the ratios of hydrocarbons to amino groups under the same conditions of the primary equivalence ratio. That is, the two phenomena appear in a multilayered way. With a rise in the primary equivalence ratio over stoichiometric conditions, the conversion rate of NH_3 to NOx decreases. At the same time, with a rise in CH_4 concentration in the fuel, the HCN produced in the reducing primary combustion zone increases and NOx emissions originating from HCN in the fuel-lean secondary combustion zone increase. Moreover, when the primary equivalence ratio rises higher, NOx production through HCN exceeds the reduction of NH_3 to N_2, and then the conversion rate rises inversely. Therefore, there is an optimum primary equivalence ratio, ϕ_p^*, where the conversion rate reaches a minimum depending on CH_4 concentration conditions, as shown in figure 8. The optimum primary equivalence ratio, ϕ_p^*, decreases and comes close to stoichiometric conditions, and its conversion rate increases with a rise in CH_4 concentration.

Figure 9 shows the correlation between ϕ_p and the CO emission concentration in two-stage combustion with the CH_4 concentration in the fuel as a parameter, when the averaged equivalence ratio at the combustor exhaust, ϕ_{ex}, is set at 0.44. The test conditions are same as the case shown in figure 8. The CO emission characteristics showed similar tendencies at any CH_4 concentration, or CO emissions had the two local maximal values except for the case of fuel containing no CH_4. At first CO emissions indicated the maximum when the primary equivalence ratio was 1.2, regardless of CH_4 concentration in the fuel. Those CO emission concentrations became higher with rises in CH_4 concentration in the cases of fuels containing CH_4. For a second time, CO emission concentration reached a maximum at each ϕ_p that was higher than 1.2 and different by CH_4 concentration. The two maximal values of CO emissions increased in direct proportion to CH_4 concentration. The certain range of the primary equivalence ratio, at which the CO emissions indicated a steep rise for the second time, was almost equivalent to that of the rising phase of the conversion rate of NH_3 to NOx, as shown in figure 8. Those certain ranges of the primary equivalence ratios drop and come close to the stoichiometric conditions with a rise in CH_4 concentration. As the CH_4 concentration increased, the quantity of supplied air to primary combustion increased under conditions of the same primary equivalence ratio and ratios of air against combustible components in fuels rose, then the local flame temperature tended to decrease. Following the decompositions of CH_4 and NH_3, HCN was produced and NH_3 was reproduced at the lower primary equivalence ratios of
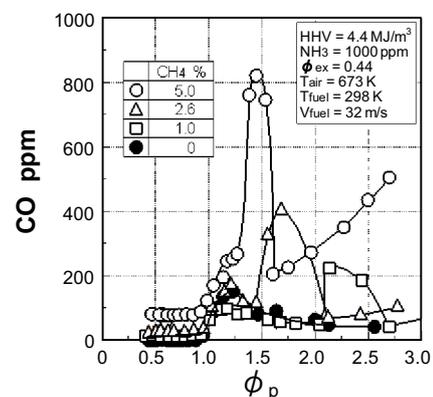

Fig.9 Effect of CH_4 concentration on CO emission characteristics in two-stage combustion (Hasegawa et al., 2001)

a reducing atmosphere. With a rise in CH_4 concentration, HCN production and NH_3 reproduction increased. The HCN and reproduced NH_3 were oxidized to NOx with certainty in the secondary combustion zone of the oxidation atmosphere. Therefore, NOx production and CO emissions increased through HCN production including NH_3 reproduction by foregoing reactions (22)-(27) with a rise in CH_4 concentration. The phenomena shown in figure 9 proved the abovementioned reaction mechanisms of NH_3 in the CO, H_2 and CH_4 mixture-fueled, two-stage combustion.

Prediction Methodology of Fuel-NOx Emissions

    NH_3 conversion through HCN.   Figure 10 rearranges the experimental data shown in figure 8 by the following equation (28). The following data, ΔC.R., shows the difference between the
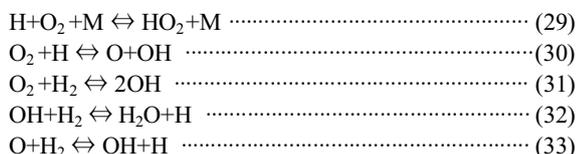
$$\Delta C.R. = C.R. - C.R._{(CH_4 = 0)} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (28)$$

conversion rate of NH_3 to NOx in the case of fuel containing each CH_4 concentration, and that in the case of fuel containing no CH_4, where $C.R._{(CH_4 = 0)}$ designates the value of C.R. in fuels with no CH_4. That is, ΔC.R. indicates the conversion rate of NH_3 to NOx through the intermediate HCN which depends on CH_4 constituent. In each CH_4 concentration condition, correlation between the primary equivalence ratio in two-stage combustion, ϕ_p, and the conversion rate difference, ΔC.R., showed a similar tendency. When the primary equivalence ratio ϕ_p was less than 1.0 (i.e., fuel-lean condition), the conversion rate difference ΔC.R. increased slightly with the rise in ϕ_p and the higher CH_4 concentration increased the values of ΔC.R.. On the other hand, when the primary equivalence ratio ϕ_p was more than 1.0 (i.e., fuel-rich conditions), the conversion rate difference of ΔC.R. decreased rapidly. After having shown each local minimal value, ΔC.R. reversely increased in proportion to ϕ_p at any CH_4 concentration. Compared with the same ϕ_p conditions, ΔC.R. tended to increase in proportion to the CH_4 concentration, too. Particularly since ΔC.R. showed the lower values than zero in the narrow range between 1.0 and 1.5 of ϕ_p, it could be said that the CH_4 content in fuel promoted the decomposition of NH_3 to N_2. In this narrower range of ϕ_p, the following overall reaction (3) of a

$$NH_3 + NO + 1/4O_2 \Leftrightarrow N_2 + 3/2H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots (3)$$
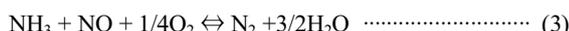
selective mutual reduction, where prompt NO and early produced fuel-NO react with NH_3 to form N_2, progress preeminently. That is, NO production through HCN promotes the NH_3 decomposition.

    On the other hand, HCN production increased with a rise in ϕ_p over stoichiometric conditions and HCN reacted with OH radicals et al. to NOx in the secondary combustion zone. When the ϕ_p was over stoichiometric mixture ratio, both the decomposition of NH_3 to N_2 and the oxidation of NH_3 to NOx through HCN proceeded. Then the C.R. took each minimum value at each appropriate primary equivalence ratio, ϕ_p^*, depending on the CH_4 concentration in fuel, as shown in figure 8. In the same way, at each CH_4 concentration, there was a peculiar primary equivalence ratio, ϕ_p', that minimized the value of ΔC.R.. And the value of ϕ_p' decreased and came close to the stoichiometric mixture ratio with a rise in CH_4 concentration. This phenomena was caused both by increment of HCN production originating from NH_3 at reducing conditions and by the selective mutual reductions of NH_3 and NO. When the CH_4 concentration became relatively higher in comparison to the H_2 concentration, the forward reacting doses of the following reactions (29)-(33) decreased markedly in the reducing reaction

$$H + O_2 + M \Leftrightarrow HO_2 + M \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (29)$$
$$O_2 + H \Leftrightarrow O + OH \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (30)$$
$$O_2 + H_2 \Leftrightarrow 2OH \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (31)$$
$$OH + H_2 \Leftrightarrow H_2O + H \quad \cdots\cdots\cdots\cdots\cdots\cdots (32)$$
$$O + H_2 \Leftrightarrow OH + H \quad \cdots\cdots\cdots\cdots\cdots\cdots (33)$$

field, the production of OH and O radicals originated from H_2 in the chain initiation reaction decreased, oxidation reactions of CH_4 and NH_3 slowed overall, and HCN production rate increased.

    Prompt NO and fuel-NO produced in the primary combustion zone of a reductive atmosphere promote the selective mutual reduction (3). Reaction (3) has an attribute where the overall reaction rate scores higher under conditions of a specific temperature, called "temperature window", and a specific equivalence ratio. The selective reduction reaction (3) generally depends on reaction temperature, NH_3/NO molar ratio in fuel, and concentrations of O_2 and H_2, and its reaction forms the specific temperature window conditions that maximize the rate of reaction (3).

    When increasing the CH_4 concentration in the fuel, the quantities of prompt NO and fuel-NO derived through HCN increase, followed by a progression of the overall reduction reaction (3). Therefore, the higher concentration of CH_4 lowered the minimum value of the conversion rate difference ΔC.R. below zero, while the peculiar primary equivalence ratio ϕ_p' was limited to the narrower range between 1.0 and 1.5 within the experimental conditions. Consequently, the ϕ_p' values varied depending on the CH_4 constituent, and simultaneously came close to the stoichiometric mixture ratio with a rise in CH_4 concentration, just as the case of ϕ_p^* in figure 8.

    With a rise in ϕ_p over 1.5, however, HCN production in the primary combustion zone substantially increased as compared with NH_3 decomposition and the NO production through HCN caused a sharp rise in ΔC.R..
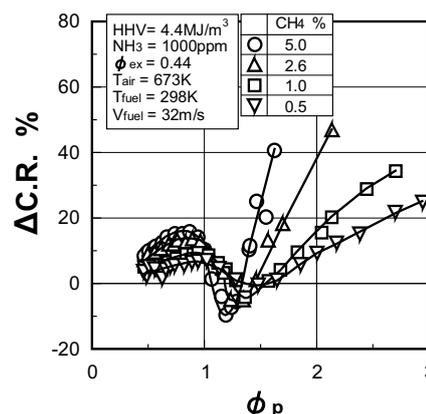

Fig.10 Effect of CH_4 concentration on difference in conversion rates between each case of fuel including CH_4 and that including no CH_4 in two-stage combustion. Data in figure 8 was rearranged.
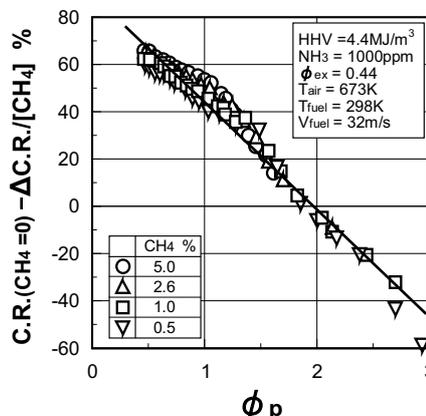

Fig.11 Prediction of relationship between CH_4 concentration in fuel and characteristics of conversion rates of NH_3 to NOx in two-stage combustion. $C.R._{(CH_4 = 0)}$; values of C.R. in cases where fuels contain no CH_4.

Predictions by approximation. In the case of typical NH_3 reduction methods with a combustion-air staging supply, it is expected that the influence of a "temperature window" on fuel-NOx production is weaker than that of NOx production through intermediate HCN. In order to make a clear correlation between CH_4 concentrations in fuels and the corresponding conversion rates, figure 11 indicates a difference value that subtracts the quotient, which is obtained by dividing each conversion rate difference Δ C.R. by the corresponding CH_4 concentration, "[CH_4]", from the value of C.R.$_{(CH_4=0)}$ in each case of ϕ_p. The calculated amounts of the vertical axis are in inverse proportion to the primary equivalence ratio of ϕ_p and it could be approximated by the following expression (34) in the range of ϕ_p

$$\text{C.R.}_{(CH_4=0)} - \Delta \text{C.R.}/[CH_4] = -46 \times \phi_p + 90 \quad \cdots\cdots (34)$$

$$\text{C.R.}_{(CH_4=0)} = f(\phi_p) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (35)$$

between 0.44 and 3.00. The ϕ_p of 0.44 is the minimum value in this case of the air-staging supply combustion, or indicates non-staging combustion.

The term of "Δ C.R./[CH_4]" means the conversion rate of NH_3 to NOx through intermediate HCN per unit CH_4 concentration and can be described by the function of ϕ_p at any CH_4 concentration in fuel. C.R.$_{(CH_4=0)}$ can be expressed without controversy as a function of the primary equivalence ratio ϕ_p as shown in figure 8. And also, the left-hand side of equation (34), "C.R.$_{(CH_4=0)}$ - Δ C.R. /[CH_4]", can be expressed as a function of ϕ_p, and expression (34) shows accurate straight-line approximation. Δ C.R. means the conversion rate NH_3 to NOx through HCN and tends to increase depending on both the CH_4 concentration and ϕ_p. Since Δ C.R./[CH_4] is "C.R.- C.R.$_{(CH_4=0)}$" per unit CH_4 concentration, "C.R.$_{(CH_4=0)}$ - Δ C.R./[CH_4]" equals to "$2 \times$ C.R.$_{(CH_4=0)}$ - C.R." in case of fuel with unit CH_4 concentration of 1 percent. When each of C.R.$_{(CH_4=0)}$ and C.R. is approximated by quadratic function of ϕ_p, leading coefficient of second-order term of approximation of C.R. is twice of that of the case of C.R.$_{(CH_4=0)}$. As a result, the coefficient of second-order term of quadratic approximation of the left-hand side of equation (34) come out even, and the equation (34) can be approximated by a linear function of ϕ_p, where the gradient is "- 46" and y-intercept is "+ 90". The standard deviation of the approximation equation (34) was within 4.8 percent.

When vertical axis of "C.R.$_{(CH_4=0)}$ - Δ C.R./[CH_4]" equals zero, conversion rates in fuel containing no CH_4 of "C.R.$_{(CH_4=0)}$" become equal to the partial conversion rates of NH_3 to NOx through HCN of "Δ C.R./[CH_4]" under the conditions where fuel contains each CH_4. In other words, Δ C.R. is in proportion to the CH_4 concentration with proportionality factor of 1.0 under the condition of 2.0 of ϕ_p and the conversion rate of NH_3 to NOx through HCN accounts for half of the total conversion rate at unit CH_4 concentration of 1 percent. And negatives of "C.R.$_{(CH_4=0)}$ - Δ C.R./[CH_4]" indicate that the conversion rates of NH_3 to NOx through HCN account for over half of the total conversion rates of NH_3 to NOx. Consequently, expressions (34) and (35) show that the conversion rate of nitrogenous compounds in the fuel to NOx could be guessed in the case where the fuel contained a CH_4 constituent at any given concentration, if experimental data on the intended gas turbine combustor was preliminarily obtained both in fuel containing no CH_4 and in a typical example of fuel containing an CH_4 at two ϕ_p conditions each.

Scope of application. When the combustor developed for the intended gasification power plant is applied to another type gasification plant, fuel-NOx emissions can be evaluated based on the abovementioned prediction technique. Additionally, in the case of the combustor development, the prediction technique can optimize the ϕ_p conditions to reduce fuel-NOx emissions in fuel containing CH_4 at any given concentration. The conversion rate of

NH_3 to NOx can be given by substituting the values of ϕ_p of the combustor and CH_4 concentration in fuel into the equations (34) and (35). Then the appropriate value of ϕ_p that minimizes C.R. could be determined depending on the CH_4 concentration of the intended fuel.

The basic principle of prediction methodology indicated by figure 11 and expression (34), is not limited to reducing combustion for fuel-NOx reduction, but it can be applied widely to the supplied-air staging combustion of CO, H_2 and CH_4 mixture fuels. As suggested by figure 7, the relation between ϕ_p and "C.R.$_{(CH_4=0)}$ - Δ C.R./[CH_4]" in fuel CO/H_2 molar ratio of 0.43 will be expected to show the same tendency as that in the case of fuel CO/H_2 molar ratio of 2.33. However, the gradient and y-intercept of the approximation (34) and the approximation function (35) are decided by the H_2 constituent in fuel without relying on fuel CO concentration, fuel calorific value and equivalence ratio, as suggested by figure 6 and 7. That is, it requires careful attention to the fact that the expression (34) could be supposed to have ranges of both the gradient and the y-intercept occupied by fuel constituents, combustion designs and exhaust temperature. The expression (35) as a function of ϕ_p exhibits some range with the fuel CO/H_2 molar ratio, as shown in figure 7, too.

On the other hand, there is no discussion with respect to pressure effects on prediction of NOx emissions. Author et al. studied pressure influence on production processes of fuel-NOx and thermal-NO in the case of CO, H_2 and CH_4 mixture fuels (for example, Xu et al., 1997). As a result, it is assumed that influences of fuel constituents on the NOx productions show the same tendency without relying on pressure, while the conversion rates of NH_3 to NO and HCN decrease with a rise in pressure. That is, the amount of intermediate HCN decreased and the fuel-NO formed by way of the HCN decreased with the rise in pressure. In other words, the dependence of the conversion of NH_3 to fuel-NO on CH_4 constituent became weaker when pressure was raised. One of the main reasons for the abovementioned pressure influence on the intermediate HCN production is that the concentration of each radical of OH, O and H, which promotes the NH_3 decomposition and NOx formation, decreases with the rise in pressure. At the same time, diffusion coefficients of such radicals decrease. Consequently, the reduction rate of NH_3 to N_2 slightly increased in the fuel-rich region of the flame. It can be concluded that both the gradient and the y-intercept of the expression (34) depend on pressure as well as combustion designs and exhaust temperature. However, it is estimated that the influence of pressure on NOx formation is lower than those of combustion designs and exhaust temperature.

The basic principle of the prediction methodology is expectantly applied to the gaseous fuels shown in table 1 and 2. Actually the prediction methodology must be applied within narrower ranges of the fuel conditions and combustion designs depending on the type and size of the gasification power plant, and therefore, the fuel-NOx emissions can be evaluated with higher accuracy. Furthermore, it is suitable for practical use of expressions (34) and (35) to adopt values of C.R. in fuels containing low concentration of CH_4 instead of C.R.$_{(CH_4=0)}$, while author is concerned only with the case of C.R.$_{(CH_4=0)}$ to examine the basic principle of prediction methodology of fuel-NOx emissions. In terms of its engineering implications, it is noteworthy that the proposed method can predict the fuel-NOx emissions and contribute to improvement of the combustion designs for fuel-NOx reduction.

CONCLUSIONS

Earlier studies have suggested advantages of the supplied-air staging two-stage combustion with reducing flame to reduce the fuel-NOx emissions in the CO, H_2 and CH_4 mixture fueled combustions. The fuel-NOx emission characteristics have emerged through experiments and full kinetic analyses in the course of development of combustion method and combustors for various gasified fuels. That is, the conversion rates of nitrogenous

compounds such as NH_3 in fuels are greatly affected by the fuel constituent and the combustion method. For example, the primary equivalence ratio ϕ_p has to be decided with respect to the CH_4 concentration particularly when adopting two-stage combustion. From the consideration about a series of experimental results in greater details through reaction kinetics once again, the basic principles of prediction methodology of the conversion rates of nitrogenous compounds can be clarified as follows;

(1) In the case of non supplied-air staging combustion of CO, H_2 and N_2 mixture fuels at any fuel calorie, the conversion rates of fuel-bound nitrogenous compounds are greatly influenced by an H_2 constituent in fuels and depend on the ratio of fuel-bound nitrogenous compounds to the combustible component of H_2 without relying on CO constituent.

(2) When adopting supplied-air staging, two-stage combustion with reducing flame into CO, H_2, a small percent CH_4 and N_2 mixture fuel to reduce fuel-NOx emissions, the conversion rates of fuel-bound nitrogenous compounds to NOx depend almost exclusively on the CH_4 concentration and ϕ_p. "ΔC.R./[CH_4]" means the conversion rate of NH_3 to NOx through intermediate HCN per unit CH_4 concentration and can be described by a function of ϕ_p at any CH_4 concentration in fuel, and C.R.$_{(CH_4=0)}$ can be expressed as a function of ϕ_p. As a result, "C.R.$_{(CH_4=0)}$ - ΔC.R./[CH_4]" can be expressed as a linear function of ϕ_p, or the basic principle of the prediction methodology of conversion rate can be established. The conversion rate of the fuel-bound nitrogenous compounds could be guessed in the case where the fuel contained a CH_4 constituent at any given concentration, if experimental data on the intended combustor was preliminarily obtained both in fuel containing no CH_4 and in a typical example of fuel containing an CH_4 at two ϕ_p conditions each.

According to the abovementioned results under atmospheric pressure conditions, the conversion rate of the fuel-bound nitrogenous compounds can be guessed in the cases of both non supplied-air staging combustion and two-stage combustion. In terms of its engineering implications, it is noteworthy that the prediction method can be applied to various fuels, as shown in table 1 and 2. The knowledge obtained here could contribute to development of the improved low-NOx combustor.

With respect to pressure effect on the prediction of NOx emissions, earlier studies by author et al. have suggested that the dependence of the conversion of NH_3 to fuel-NO on CH_4 constituent became weaker when pressure was raised. Therefore, it can be expected that the gradient and the y-intercept of the expression (34) depend slightly on pressure. It needs further consideration about pressure influence on prediction of NOx emissions under higher-pressure conditions.

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