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Full Length Research Paper

Kinetic analysis of nitric oxide reduction using biogas as reburning fuel

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Biogas was suggested more suitable as reburning fuel to reduce NO emission and Miller-Bowan's mechanism was performed to analyze the effect of reaction environment in the process of biogas reburning. Results show that the NO reduction efficiency increased with the increase of hydrocarbon in biogas, reburning fuel ratio, initial NO concentration and residence time. When initial NO concentration reached 700 µl/l or residence time reaches 2 s, the dependence on initial NO concentration weakened greatly. NO reduction reached maximum at 1200 – 1400 K and enhanced abruptly at the stoichiometric ratio of 0.85 with the decrease of stoichiometirc ratio. The investigations indicated the optimal biogas reburnning technology potential to reduce NO pollution.

Key word: Biomass, biogas, kinetic analysis, modeling, nitric oxide, reburning.

INTRODUCTION

Emission of nitric oxide (NO) from coal combustion continues to be a significant environmental threat, which is recognized as the source of acid rain, photochemical smog and the destruction of ozonosphere. Among the recent developments for technologies of reducing NO, reburning is commercially available, and is capable of providing 50 - 85% NO reduction has been demonstrated as a practical NO reduction method by the application in a full-scale boiler of Mitsubishi until 1983 (Smoot et al., 1998). The overall process of reburning in furnace is divided into three zones; primary zone, reburning zone and burnout zone. NO forms in the first primary zone and then react with reburning-fuel in the second reburning zone to form HCN or N_2; finally, the residual fuel completes its combustion in the third burnout zone with the addition of air. Coal and natural gas have been studied as the conventional reburning fuel widely (Dimitriou et al., 2003; Hampartsoumian et al., 2003; Han et al., 2003; Sen et al., 2007; Su et al., 2007; Dagaut and Lecomte, 2003; Zarnitz and Pisupati, 2007).

With the aggravation of global greenhouse effect, biomass has been focused as a renewable fuel without CO_2 addition, and researches (Maly et al., 1999; Harding and Adams, 2000) show that the efficiency of NO reduction through biomass reburning is higher than coal reburning and natural gas reburning. The proximate analysis and elemental analysis of different biomass in Table 1 show that the volatile content in biomass is mostly higher than 70% (w/w), but the nitrogen content is low; therefore biomass is generally acknowledged a perfect reburning fuel to reduce NO pollution (Harding and Adams, 2000; Vilas et al., 2004). However, high ash and chlorine content in biomass leads to severe fouling and deposition problem in furnace. Consequently, Zhi-lin et al. (2006) and Duan et al. (2007) suggested biogas from biomass as reburning fuel and Pisupati and Bhalla (2008) has proved that results from the kinetic simulation is consistent with experiments.

The efficiency of NO reduction is limited to the reaction environment in reburning zone. To optimize environmental factors, detailed reaction mechanism loaded on a PSR computer code (Glarborg et al., 1986) is performed to analyze the effects of biogas components, reburning fuel ratio, temperature, stoichiometric ratio, initial NO concentration, residence time and role of moisture on NO reduction efficiency.

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Table 1. Proximate analysis and elemental analysis of biomass.

Biomass	Proximate analysis (%, w/w)			Elemental analysis (%, w/w)				
	M_{ad}	A_{ad}	V_{ad}	C_{ad}	H_{ad}	N_{ad}	O_{ad}	S_{ad}
Wheat straw	6.36	8.84	67.68	41.64	4.23	0.43	38.77	0.08
Corn stalk	3.70	6.30	72.62	44.42	4.95	0.57	41.25	0.11
Corncob	3.68	2.88	77.72	44.58	4.40	0.28	45.45	0.01
Sawdust	3.86	3.01	73.34	45.83	4.94	0.92	39.41	0.12

Table 2. Reactions referring to nitrogen species.

Number of reactions	Reaction equations	*A* (cm^3/mol.s.K)	*β* (1)	*E* (cal/mol)
151	$CH + N_2 \rightarrow HCN + N$	3.00×10^{11}	0.00	13600
153	$CH_2 + N_2 \rightarrow HCN + NH$	1.00×10^{13}	0.00	74000
156	$C + NO \rightarrow CN + O$	6.60×10^{13}	0.00	0
157	$CH + NO \rightarrow HCN + O$	1.10×10^{14}	0.00	0
158	$CH_2 + NO \rightarrow HCNO + H$	1.39×10^{12}	0.00	100
159	$CH_3 + NO \rightarrow HCN + H_2O$	1.00×10^{11}	0.00	15000
160	$CH_3 + NO \rightarrow H_2CN + OH$	1.00×10^{11}	0.00	15000
162	$^1CH_2 + NO \rightarrow HCN + OH$	2.00×10^{13}	0.000	0
188	$HO_2 + NO \rightarrow NO_2 + OH$	2.11×10^{13}	0.00	-479
199	$HNCO + H \rightarrow NH_2 + CO$	2.00×10^{13}	0.00	3000
216	$NH_2 + NO \rightarrow NNH + OH$	6.4×10^{15}	0.25	0
217	$NH_2 + NO \rightarrow N_2 + H_2O$	6.2×10^{15}	0.25	0
232	$N + NO \rightarrow N_2 + O$	3.27×10^{12}	0.30	0

METHODS

Kinetic mechanism and modeling environment

Miller and Bowman (1989) demonstrated the detailed mechanism on the formation and reduction of NO in the reburning process, which has been validated by many researchers (Skottene and Rian, 2007; Guo and Smallwood, 2007; Giles et al., 2006; Shoji et al., 2005). Consequently, Miller and Bowman's mechanism is selected as the calculation dynamics model. The kinetic numeration is carried out in the PSR environment of Sandia National Laboratory.

Reactions mainly referring to nitrogen species are shown in Table 2 and the characters (*A*, *β*, *E*) are defined by Arrhenius equation:

$$\kappa = AT^{\beta}\exp(-E/RT) \tag{1}$$

Where the pre-exponential factor *A*, the temperature *β*, and the activation energy *E* are specified.

Characteristics parameters

Biogas from biomass is mainly composed of CO, CO_2, H_2 and small molecule hydrocarbons (Zhi-lin et al., 2006), shown in Table 3.

The composition of flue gas from primary zone is calculated at excess air ratio of 1.2, and analysis of coal in primary zone is shown in Table 4.

The reburning parameters are defined as following:

Reburning fuel ratio:

$$\lambda = \frac{\text{Heat released in primary zone}}{\text{Heat released in primary zone+Heat released in secondary zone}} \tag{2}$$

Excess air ratio:

$$\phi = \frac{\text{Practical oxygen content}}{\text{oxygen content at stoichiometric ratio}} \tag{3}$$

Efficiency of NO reduction:

$$\eta = \frac{\text{Concentration of NO at inlet of reburnig zone- concentration of NO at oulet}}{\text{Concentration of NO at the inlet of reburnig zone}} * 100\% \tag{4}$$

RESULTS AND DISCUSSION

Effects of biogas components, excess oxygen ratio and reburning fuel ratio on the efficiency of NO reduction

Excess oxygen ratio is the most important factor affecting the reduction of NO which is shown in Figure 1 at diffe-

Table 3. Components of biogas from biomass.

Species	CO_2	CO	H_2	CH_4	C_2H_2	C_2H_4	C_3H_8
Content (%, v/v)	27.0	35.0	14.0	13.0	6.50	3.25	1.25

Table 4. Proximate analysis, elemental analysis and calorific value of coal.

Proximate analysis (%, w/w)			Elemental analysis (%, w/w)					Calorific value (kj/kg)
M_{ar}	A_{ar}	V_{daf}	C_{ar}	H_{ar}	N_{ar}	O_{ar}	S_{ar}	$Q_{net.ar}$
8.00	24.7	6.23	61.81	1.57	0.84	2.71	0.84	21248

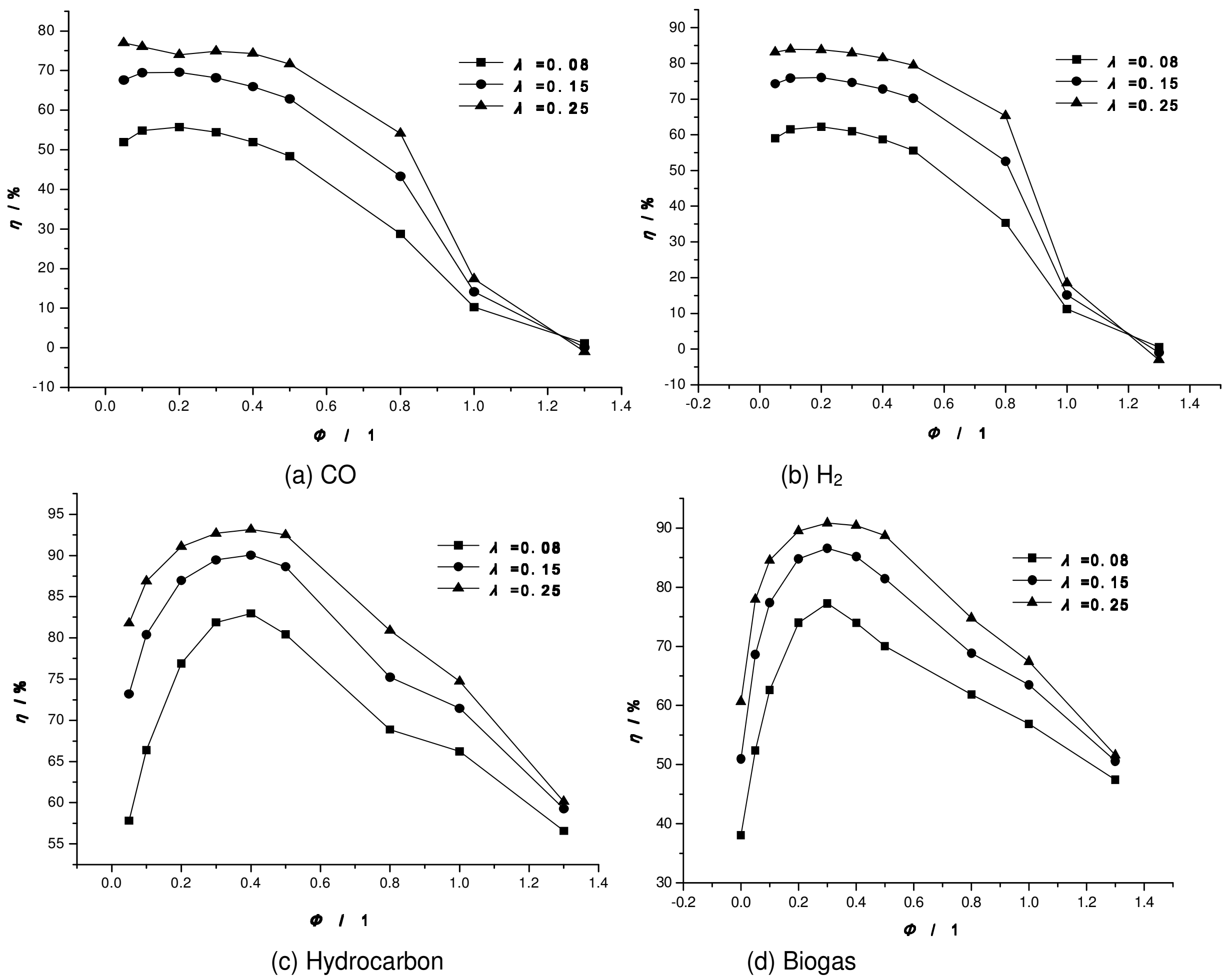

Figure 1. Effect of oxygen content and reburn fuel ratio on NO reduction for different reburning fuels.

rent reburning fuel ratio and the efficiency of biogas reburning is compared with H_2, CO and hydrocarbon to demonstrate the effects of biogas components. In this condition, it is selected at temperature of 1473 K, initial NO concentration of 1000 μl/l, residence time of 1 s. The components of hydrocarbon are determined as the ratio of CH_4, C_2H_2, C_2H_4 and C_3H_8 in Table 3.

Figure 1 shows that the efficiency of NO reduction increases with increasing of reburning fuel ratio for all the reburning fuel but it is different for the effect of excess oxygen ratio. At high excess oxygen ratio, hydrocarbon and biogas can still maintain high efficiency of NO reduction, compared with H_2 and CO. Because in the process of reburning, hydrocarbons play a key role to

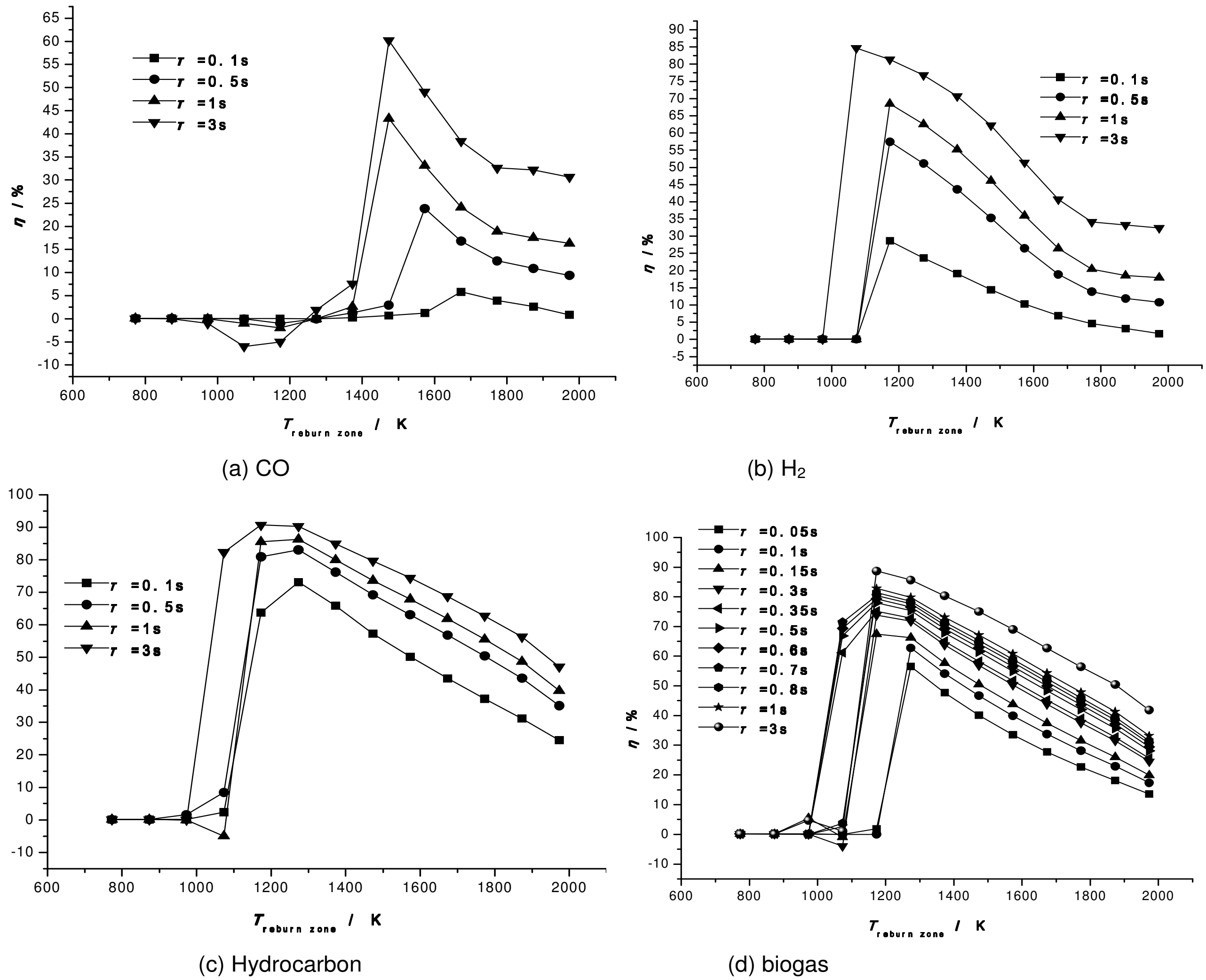

Figure 2. Effect of temperature on NO reduction for different reburning fuels.

reduce NO and the free radicals (CH, CH_2, and CH_3) from decomposition of hydrocarbon directly affect the NO reduction seen from the reactions in Table 2. Consequently, the species of hydrocarbon in biogas dominate the efficiency of NO reduction, and increasing of non-hydrocarbon species in biogas weakens the efficiency of reburning, which is consistent with the results of Pisupati and Bhalla (2008).

With the decrease of oxygen concentration, the reducing atmosphere is strengthened and then the efficiency of CO and H_2 reburning increases when the excess oxygen ratio is lower than 0.4; the efficiency is tended to be stable. This is similar to the results of Glarborg et al. (2000).

However, compared with non-hydrocarbon reburning for biogas and hydrocarbon reburning, relation between the efficiency and oxygen concentration follows the parabolic law. The efficiency of NO reduction reaches maximum at the excess air ratio of 0.4 - 0.6. Bilbao et al. (1994) used CH_4 as reburning fuel, and obtained the maximum efficiency at oxygen concentration 1.5% (v/v, excess oxygen ratio = 0.44), located in our calculated scale (0.4 - 0.6).

Effects of temperature in reburning zone

Arrhenius equation (Equation 1) shows the important role of temperature in the reburning process and Figure 2 demonstrates the effects of temperature and residence time for different reburning fuel. These conditions are at excess oxygen ratio of 0.85, reburning fuel ratio of 15% and initial NO concentration of 1000 μl/l.

At lower temperature, the efficiency of NO reduction is negligible and when temperature reaches up to the critical temperature, the efficiency begins to increases abruptly. With the continuous increase of temperature, NO will regenerate by thermal NO or promote NO to weaken the efficiency of NO reduction. With the increase of residence time, the critical temperature is lower, and

Table 5. Optimum temperature scale for different reburning fuel.

Reburning fuel	Optimum temperature scale (K)
CO	1500 - 1700
H_2	1100 - 1200
Hydrocarbon	1200 - 1400
Biogas	1250 - 1400

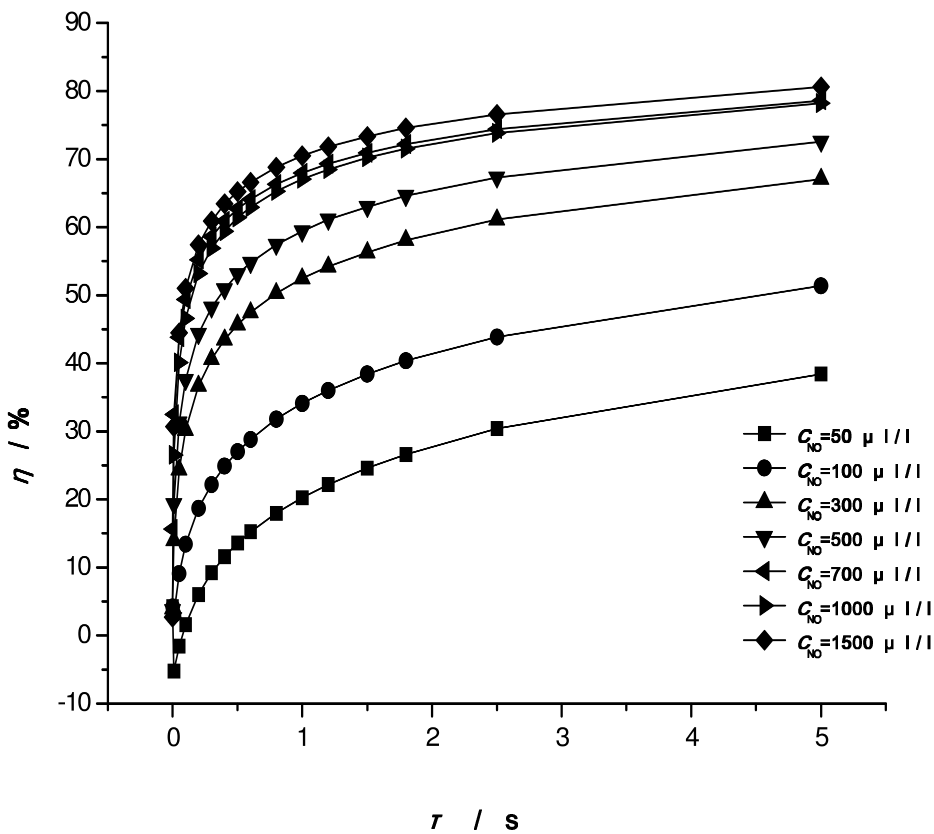

Figure 3. Effect of residence time and initial NO concentration on NO reduction.

when residence time is shorter than 0.1s, the efficiency of CO or H_2 is very low, which further emphasizes that hydrocarbon play more important role than nonhydrocarbon species.

The calculated results show that there is an optimum temperature scale, and under this condition, the scale for different species is shown in Table 5. Dagaut's results also show the best temperature scale is 1200-1300K for hydrocarbon reburning (Dagaut and Lecomte 2003).

Compared with CO reburning, the optimum temperature scale for H_2, hydrocarbon and biogas is lower. It is suggested that H_2 and hydrocarbon dissociate to form high activity free radicals like H, CH and CH_2, and according to the reactions 151 - 153 in Table 2; these free radicals can not only reduce NO but also promote the decomposition of N_2 to form fresh NO.

Effects of initial NO concentration, residence time and moisture concentration

In the process of biogas reburning, the effects of residence time and initial NO concentration are shown in Figure 3, and the condition is at excess oxygen ratio of 0.85, reburning fuel ratio of 15% and reburning temperature of 1473 K.

With the increase of residence time, the efficiency of NO reduction enhances, however when the residence time reaches 2 s, the efficiency will not change largely, and it consists with the results of previous researches (Maly et al., 1999; Harding and Adams, 2000; Duan et al., 2007). Similar to residence time, at the beginning increase of initial NO concentration will improve the efficiency, but after the initial NO concentration exceeding

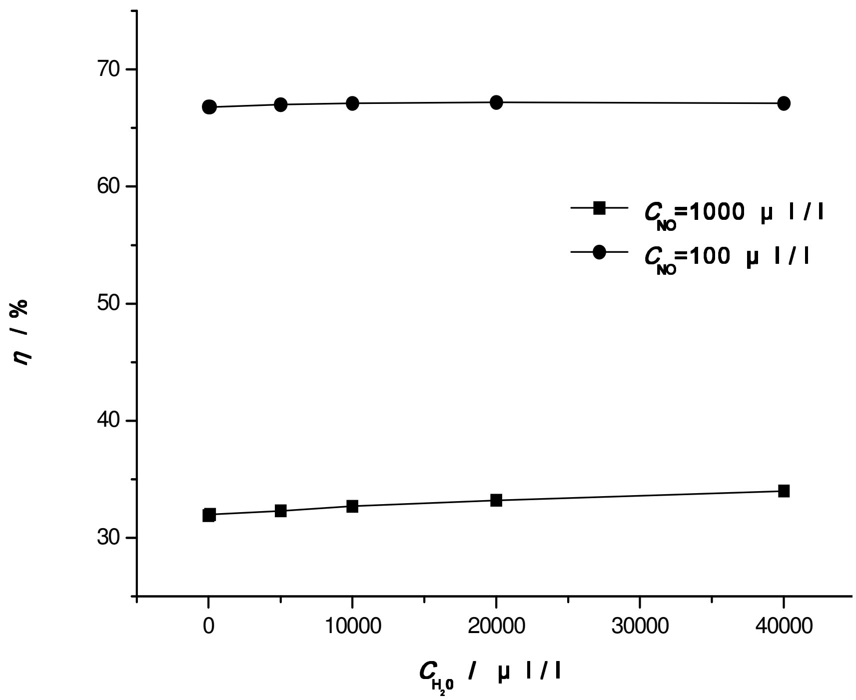

Figure 4. Effect of moisture content on NO reduction.

700 μl/l, the dependence of NO reduction on initial NO concentration is weakened greatly.

Figure 4 shows the efficiency of moisture concentration on NO reduction at initial NO concentration of 1000 and 100 μl/l, and it demonstrates that the effect of moisture is negligible. Vilas's analysis on adding moisture in the process of biomass reburning has concluded the same result (Vilas et al., 2004).

Conclusion

In this paper, kinetic modeling was performed to analyze the effects of biogas components, reburning fuel ratio, temperature, stoichiometric ratio, initial NO concentration, residence time and moisture on the NO reduction efficiency in the process of biogas reburning. Compared with the previous experimental results, it is concluded that, the efficiency of NO reduction increases with the increase of reburning fuel ratio, and biogas containing more hydrocarbon is more efficient on NO reduction. At excess oxygen of 0.4 - 0.6 and reburning temperature of 1250 - 1400 K, the efficiency of biogas reburning is maximum. When the initial NO concentration reaches 700 μl/l or the residence time reaches 2 s, the dependence of NO reduction on initial NO concentration and residence time is weakened greatly. The addition of moisture weakens NO reduction trivially. The investigations provide a detailed description of biogas reburning which indicates that the optimal biogas reburnning technology has potential to reduce the emission of NO.

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REFERENCES

Bilbao R, Millera A, Alzueta MU (1994). Influence of the Temperature and Oxygen Concentration on NOx Reduction In The Natural Gas Reburning Process Ind. Eng. Chem. Res. 33 : 2846-2852.

Dagaut P, Lecomte F (2003). Experimental and kinetic modeling study of the reduction of NO by hydrocarbons and interactions with SO2 in a JSR at 1atm*. Fuel, 82: 1033-1040.

Dimitriou DJ, Kandamby N, Lockwood FC (2003). A mathematical modelling technique for gaseous and solid fuel reburning in pulverised coal combustors. Fuel, 82: 2107-2114.

Duan J, Luo YH, Yan NQ, Chen Y (2007). Effect of Biomass Gasification Tar on NO Redcuction by Biogas Reburing. Energy Fuels, 21: 1511-1516.

Giles DE, Som S, Aggarwal SK (2006). NOx emission characteristics of counterflow syngas diffusion flames with airstream dilution. Fuel, 85: 1729-1742.

Glarborg P, Kee RJ, Grcar JF, Miller JA (1986). PSR: a FORTRAN program for modeling well-stirred reactors, Sandia Report SAND86-8209.

Glarborg P, Kristensen PG, Dam-Johansen K (2000). Nitric Oxide Reduction by Non-hydrocarbon Fuels. Implications for Reburning with Gasification Gases. Energy Fuels 14: 828 -838.

Guo H, Smallwood GJ (2007). A numerical investigation on NOX formation in counterflow n-heptane triple flames. Int. J. Thermal Sci. 46: 936-943.

Hampartsoumian E, Folayan OO, Nimmo W, Gibbs BM (2003). Optimisation of NOx reduction in advanced coal reburning systems

and the effect of coal type[small star, filled]. Fuel, 82: 373-384.
Han X, Wei X, Schnell U, Hein KRG (2003). Detailed modeling of hybrid reburn/SNCR processes for NOX reduction in coal-fired furnaces. Combust. Flame, 132: 374-386.
Harding NS, Adams BR (2000). Biomass as a reburning fuel: a specialized cofiring application. Biomass Bioenergy, 19: 429-445.
Maly PM, Zamansky VM, Ho L, Payne R (1999). Alternative fuel reburning. Fuel 78: 327-334.
Miller JA, Bowman CT (1989). Mechanism and modeling of nitrogen chemistry in combustion. Progr. Energy Combust. Sci. 15: 287-338.
Pisupati SV, Bhalla S (2008). Numerical modeling of NOx reduction using pyrolysis products from biomass-based materials. Biomass Bioenergy 32: 146-154.
Sen L, Tongmo X, Qulan Z, Houzhang T, Shien H, Hongli H (2007). Optimization of coal reburning in a 1MW tangentially fired furnace. Fuel 86: 1169-1175.
Shoji M, Yamamoto T, Tanno S, Aoki H, Miura T (2005). Modeling study of homogeneous NO and N2O formation from oxidation of HCN in a flow reactor. Energy 30: 337-345.
Skottene M, Rian KE (2007). A study of NOx formation in hydrogen flames. Int. J. Hydrogen Energy, 32: 3572-3585.
Smoot LD, Hill SC, Xu H (1998). NOx control through reburning. Progr. Energy Combust. Sci. 24: 385-408.
Su S, Xiang J, Sun L, Zhang Z, Sun X, Zheng C (2007). Numerical simulation of nitric oxide destruction by gaseous fuel reburning in a single-burner furnace. Proc. Combust. Inst. 31: 2795-2803.
Vilas E, Skifter U, Jensen AD, Lopez C (2004). Experimental and Modeling Study of Biomass Reburning. Energy Fuels, 18: 1442-1450.
Zarnitz R, Pisupati SV (2007). Evaluation of the use of coal volatiles as reburning fuel for NOx reduction. Fuel, 86: 554-559.
Zhi-lin F, Jun Z, Chang-dong S, Xiao-feng L, Yi-qian X (2006). Experimental Study of NO Reduction through Reburning of Biogas. Energy Fuels, 20: 579-582.