Modeling and Simulation on NO$_x$ and N$_2$O Formation in Co-combustion of Low-rank Coal and Palm Kernel Shell

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Abstract

NO$_x$ and N$_2$O emissions from coal combustion are claimed as the major contributors for the acid rain, photochemical smog, green house and ozone depletion problems. Based on the facts, study on those emissions formation is interest topic in the combustion area. In this paper, theoretical study by modeling and simulation on NO$_x$ and N$_2$O formation in co-combustion of low-rank coal and palm kernel shell has been done. Combustion model was developed by using the principle of chemical-reaction equilibrium. Simulation on the model in order to evaluate the composition of the flue gas was performed by minimization the Gibbs free energy. The results showed that by introduced of biomass in coal combustion can reduce the NO$_x$ concentration in considerably level. Maximum NO level in co-combustion of low-rank coal and palm kernel shell with fuel composition 1:1 is 2,350 ppm, low enough compared to single low-rank coal combustion up to 3,150 ppm. Moreover, N$_2$O is less than 0.25 ppm in all cases.

Keywords: low-rank coal, N$_2$O emission, NO$_x$ emission, palm kernel shell

1. Introduction

N$_2$O is a sharp green house gas. It is responsible for the destruction of ozone in the atmosphere. The concentration of N$_2$O in atmosphere increases at the rate of 0.2-0.4% per year. On the other hand, NO$_x$ emissions are also a major environmental problem because they have been shown to contribute to the formation of acid rain and photochemical smog (Förtsch, 1998). In recent years, intensive researches that worked on the mechanism of formation and decomposition of N$_2$O and NO$_x$ have been carried out in over the world. Moritomi *et al.* (1991) and Amand and Andersson (1989) correlated the N$_2$O emission to the fuel ratio of various fuels. Boemer *et al.* (1993) have considered such factors as coal rank, excess air ratio and temperature as the most important parameters influencing N$_2$O and NO$_x$ emissions in coal combustion (Shen *et al.,* 2003).

Moreover, the effects of co-combustion of coal and biomass on the emissions formation have also been studied by Shen *et al.* (2003) and Ross *et al.* (2002). Several mechanism and kinetics of N$_2$O and NO$_x$ formation and reduction have been proposed (Shen *et al.*, 2003; Förtsch, 1998; Li *et al.*, 1998). Advanced kinetic reaction models have been developed that describe the process of devolatilisation, volatiles conversion and char burnout.

This paper deals with the theoretical study on NO$_x$ and N$_2$O formation in co-combustion of low-rank coal and palm kernel shell (PKS) as function of air/fuel ratio, inlet air temperature and reactor pressure.
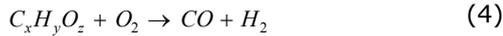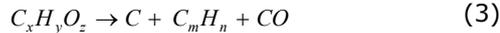
2. Kinetic Model of Combustion

Modeling of coal and biomass combustion is usually based on the assumption that the conversion of coal/biomass can be divided into three steps: pyrolysis, combustion of volatiles and char burn-out. Pyrolysis can be regarded as a two-stage process: primary pyrolysis and secondary pyrolysis. During primary pyrolysis, coal/biomass decomposes releasing volatile matter that, afterward, undergoes secondary pyrolysis.

The primary pyrolysis process is approximated by the single reaction (Förtsch *et al.*, 1998):

$$RF \rightarrow C + T + G \qquad (1)$$

RF denotes raw fuel (coal/biomass, daf): *C*, *T* and *G* represent the main products of pyrolysis: char, tar and gas. Char is assumed to be pure carbon; gas is a mixture of CO, CO$_2$, H$_2$, H$_2$O and a light hydrocarbon: C$_m$H$_n$, represented by C$_2$H$_4$. Tar fraction is assumed as C$_x$H$_y$O$_z$ with an H/C molar ratio of 1.1 and an O/C molar ratio equal to the parent coal/biomass.

After being released, the volatile matter undergoes secondary reactions, especially tars. The secondary reactions of tar are modeled by considering three competing reactions producing soot, hydrogen, light hydrocarbons and carbon monoxide (Förtsch *et al*., 1998):

$$C_xH_yO_z \rightarrow C + H_2 + CO \qquad (2)$$

$$C_xH_yO_z \rightarrow C + C_mH_n + CO \qquad (3)$$

$$C_xH_yO_z + O_2 \rightarrow CO + H_2 \qquad (4)$$

Since there exists no boundary layer on the soot particle surface, soot is treated as a gaseous in combustion. Therefore, the burnout of soot and char particles is (Förtsch *et al*., 1998):

$$C + \frac{1}{2}O_2 \rightarrow CO \qquad (5)$$

3. Fuel-Nitrogen Evolution, NO$_x$ Formation and Reduction

In coal/biomass combustion, the major part of NO$_x$ emissions arise from fuel-bound nitrogen released during different stages of combustion:
a. primary pyrolysis; reaction (1),
b. secondary pyrolysis of tar; reactions (2)-(4),
c. soot and char burnout; reaction (5).

Each of the pyrolysis products contains nitrogen, the distribution of which depends on the nitrogen functional groups in the particular fuel, on fuel properties and pyrolysis conditions. Tar nitrogen is released as HCN during secondary reactions of tar with a certain amount of nitrogen remaining in the soot. The rate of volatile nitrogen release is assumed to follow the rate of primary pyrolysis; the rates secondary reactions of tars; and the rate of soot combustion. The release of char nitrogen during char combustion is enhanced in the first stages of char combustion.

Reactions of the nitrogen-containing species taking place in the gas phase are very complex. The NO$_x$ reaction scheme is shown in Fig. 1. By taking in considerations the CN subsystem, represented by HCN, and the NH$_i$ subsystem, comprising all highly reactive nitrogen-containing intermediate species (Förtsch *et al.,* 1998).

Decay of the CN subsystem is initiated by the attack of oxygen-containing species (Förtsch *et al.,* 1998):

$$HCN + O_x \rightarrow NH_i + \ldots \qquad (6)$$

For the subsequent conversion of NH$_i$ species, oxidation of this species to form NO and reduction of NO are considered (Förtsch *et al.,* 1998):

$$NH_i + O_x \rightarrow NO + \ldots \qquad (7)$$
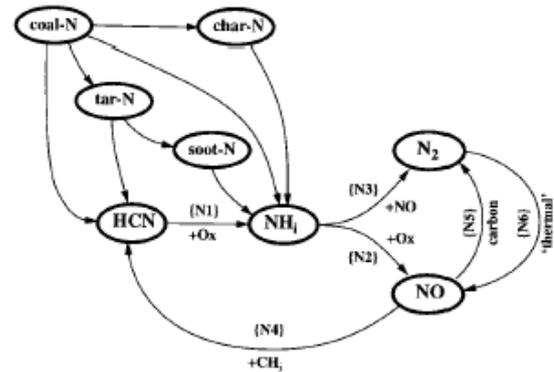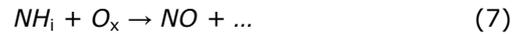$$NH_i + NO \rightarrow N_2 + \ldots \qquad (8)$$

Figure 1. Reaction scheme describing conversions of nitrogenous species

Furthermore, the model is considered as the heterogeneous reduction of NO and N$_2$O at carbonaceous surface:
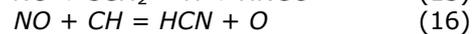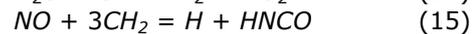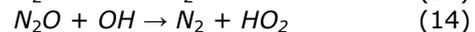
$$NO + C \rightarrow \tfrac{1}{2} N_2 + CO \qquad (9)$$
$$N_2O + C \rightarrow N_2 + CO \qquad (10)$$
$$2N_2O + C \rightarrow 2N_2 + CO_2 \qquad (11)$$

The reduction of NO by soot is more efficient than that of char.

Also, thermal NO mechanism is taken into account (Förtsch *et al.,* 1998):

$$N_2 + O_x \rightarrow 2 NO + \ldots \qquad (12)$$
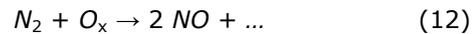
The influence of biomass on reduction of NO$_x$ and N$_2$O may be initiated by some reductive radicals that produced in high temperature pyrolysis (Donghee *et al*., 1999; Larfeldt and Leckner, 2000):

$$N_2O + H \rightarrow N_2 + OH \qquad (13)$$
$$N_2O + OH \rightarrow N_2 + HO_2 \qquad (14)$$
$$NO + 3CH_2 = H + HNCO \qquad (15)$$
$$NO + CH = HCN + O \qquad (16)$$

4. Modeling and Simulation Procedure

Modeling and simulation were performed by using Aspen Plus, a commercial process simulator. In this simulator, decomposition and combustion processes took place in the Yields and Gibbs Reactors, respectively. Decompo-sition is addressed to decompose

the fuel into its elements because the Gibbs Reactor can not detect the conventional species such as coal or PKS. Energy for decomposition is supplied automatically from combustion by connecting the Yields and Gibbs Reactors using an energy line as shown by dashed line in Fig. 2.

The compositions of the flue gas in combustion process were evaluated by minimization of the Gibbs free energy using the following equations:

$$\frac{\Delta G}{RT} = \frac{\Delta G^0 - \Delta H^0}{RT_0} + \frac{\Delta H^0}{RT} + \frac{1}{T}\int_{T_0}^{T}\frac{\Delta C_p}{R}dT$$

$$-\int_{T_0}^{T}\frac{\Delta C_p}{R}\frac{dT}{T} \tag{17}$$

$$\frac{\Delta G}{RT} = -\ln K \tag{18}$$

$$\prod_i (y_i \phi_i)^{v_i} = \left(\frac{P}{P^0}\right)^{-v} K \tag{19}$$

Fugacity coefficient in the model was estimated using Peng-Robinson equation of state:

$$\ln\phi_i = \frac{B_i}{B}(Z-1) - \ln(Z-B) + \frac{A}{4,828 B}$$

$$\left[\frac{B_i}{B} - \frac{2}{a\alpha}\sum_j y_j (a\alpha)_{ij}\right]\ln\left[\frac{Z+2,414B}{Z-0,41B}\right] \tag{20}$$

where ΔG = Gibbs free energy (J/mol)
  ΔH = enthalpy (J/mol)
  T = temperature (K)
  R = gas constant (J/mol K)
  C_p = heat capacity (J/mol K)
  K = equilibrium constant
  y_i = equilibrium composition of species i
  ϕ_i = fugacity coefficient of species i
  v_i = coefficient of stoichiometry
  P = pressure (atm)
  a, A, B, α = constants of Peng Robinson equation of state.

Table 1 shows the data of proximate and ultimate analysis for coal and PKS used in this study.

5. Results and Discussion

5.1. Coal combustion

Profiles of N_2O and NO_x in coal combustion is shown in Fig. 3, it indicates that the maximum NO emission in single coal combustion appears at air to fuel ration about 9.18 kg/kg. At this point, NO emission

reaches level of 3,150 ppm. Meanwhile, the maximum NO_2 is about 4.75 ppm at air to fuel ratio 12.75-13.65 kg/kg. The lowest level of emission is presented by N_2O which shows a value less than 0.25 ppm over the observation range. Decrease in NO by increase of oxygen after reached the maximum level is predicted by NO reduction phenomenon (Liu *et al*., 1999):

$$NO + O_2 \rightarrow NO_2 + O \tag{21}$$

The above phenomenon is also supported by increase in NO_2 concentration during the combustion. Another possibility for reduction of NO is initiated by soot as was explained in reaction (9). Adiabatic combustion temperature range in this case is 1,477-2,188 K. those All simulation data were achieved at the equilibrium conversion and the minimum total Gibbs energy.

5.2. PKS combustion

Combustion of single palm shell exhibits the same pattern of emissions with single coal combustion, however the emission level is significantly low especially for NO emission as shown in Fig. 4. For this case, adiabatic combustion temperature range is 1,390-1,867 K. Based on the facts that the nitrogen content in coal (0.48%) and PKS (0.30%) as listed in Table 1, and combustion temperature is different, therefore it can be proposed that the NO_x emissions are come from fuel and thermal NO_xs. The same behavior is also proposed for the N_2O emission. In other word, both fuel and thermal NO_xs give a contribution for emissions.

5.3. Co-combustion of coal and PKS

As expected, introduce of biomass in co-combustion can significantly reduce the NO emission and slightly reduce the NO_2 and N_2O emissions (by compared the data in Fig. 5 with the data in Fig. 3). The effect of biomass on reduction of NO_x and N_2O has been described in reactions (13-16). Since the reductions of NO_x and N_2O are caused by reductive radical reactions, then the patterns for NO and NO_2 are depart from single coal or single PKS combustion. All the emission levels and temperatures in co-combustion lie between single coal and single palm shell combustions. Fig. 5 reflects the effectiveness of biomass in reduction of emissions in co-combustion. Weight ratio of coal to palm shell in this study is 1:1. Range of adiabatic combustion temperature for co-combustion is 1,132-2,094 K.
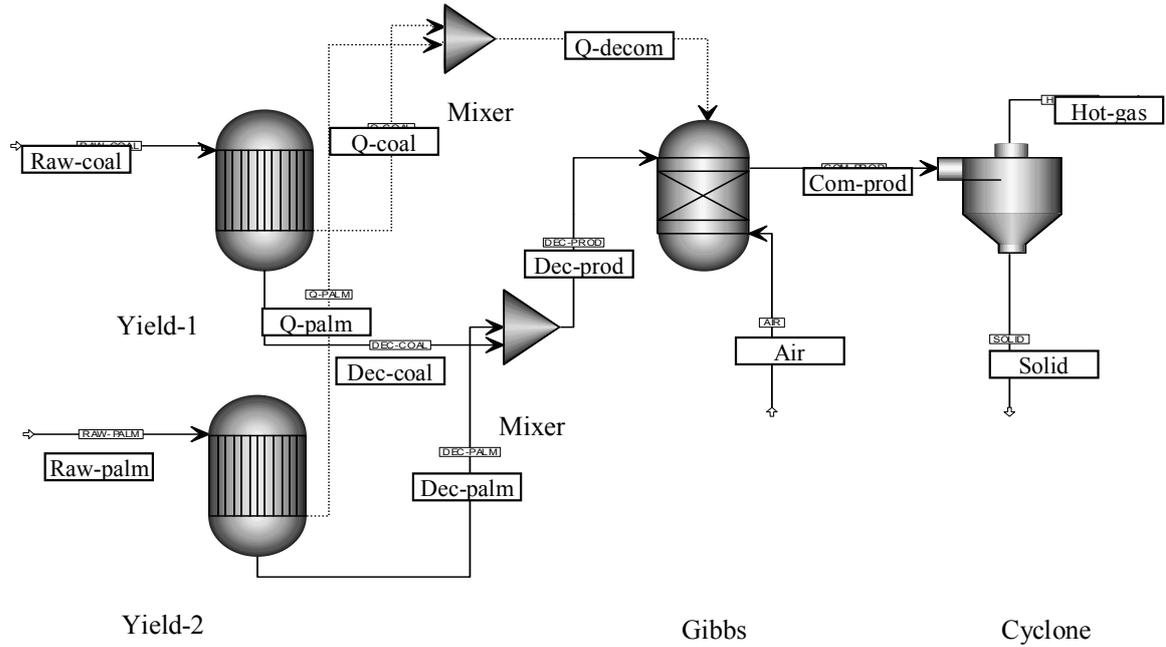
Figure 2. Flow diagram of combustion process in ASPEN PLUS Simulator

Table 1. Proximate and ultimate analysis data for low-rank coal and PKS

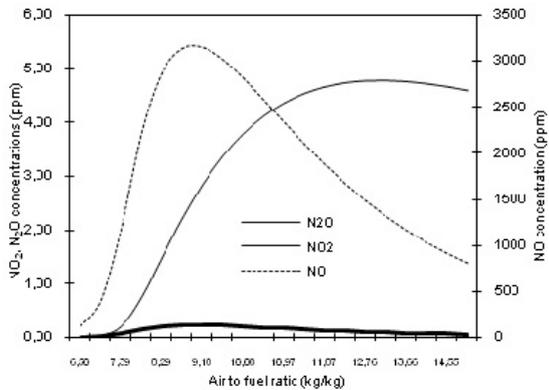|	Unit (adb)[*)]	Low-rank coal	PKS
Proximate			
Moisture	%	5.83	4.30
Ash	%	5.40	2.63
Volatile Matter	%	46.00	73.65
Fixed Carbon	%	42.77	19.42
Ultimate			
Carbon	%	60.65	29.32
Hydrogen	%	5.75	5.88
Nitrogen	%	0.48	0.30
Total Sulphur	%	0.38	0.13
Oxygen	%	27.34	61.74
Calorific Value	kcal/kg	5,904	4,865

[*)]adb = air dried base

Figure 3. NO_x and N_2O emissions as function of air to fuel ratio in single coal combustion
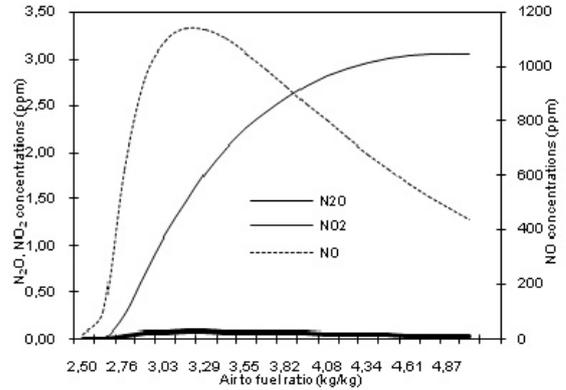

Figure 4. NO_x and N_2O emissions as function of air to fuel ratio in single palm shell combustion

It should be noted that all the above simulations are performed at pressure of 1 atm and inlet air temperature of 298 K.

Moreover, in order to observe the influence of the reactor pressure on emissions in co-combustion, simulation was conducted at several pressure levels as presented by Fig. 6.

It is clearly shown that NO tends to slow down by increase of pressure, while NO_2 and N_2O provide the opposite behavior. This fact describe that pressurised combustor is more effective in reduce of NO, the major part of emissions. In this part, simulation was carried out at air to fuel ratio 5.21 kg/kg, air inlet temperature 298 K and similar fuel composition.
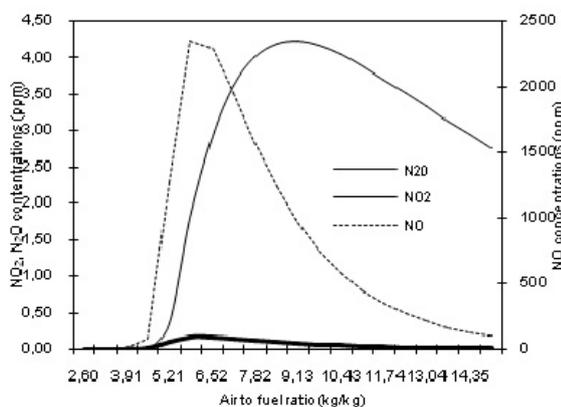

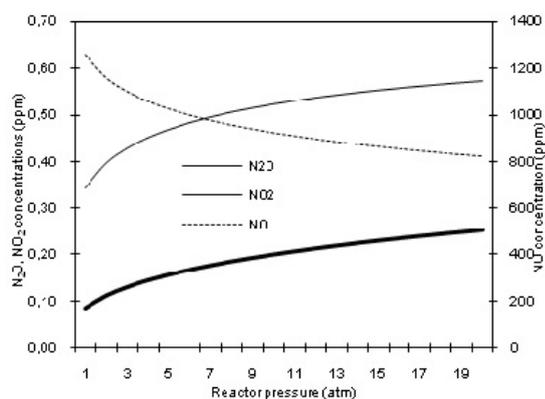**Figure 5.** NO_x and N_2O emissions as function of air to fuel ratio in co-combustion

Figure 6. NO_x and N_2O emissions as function of reactor pressure in co-combustion

Finally, increase of air inlet temperature causes the sharp increase of NO and slight increase of NO_2 and N_2O. Higher of air inlet temperature may contribute higher temperature in combustor since the combustion conducted adiabatically. This

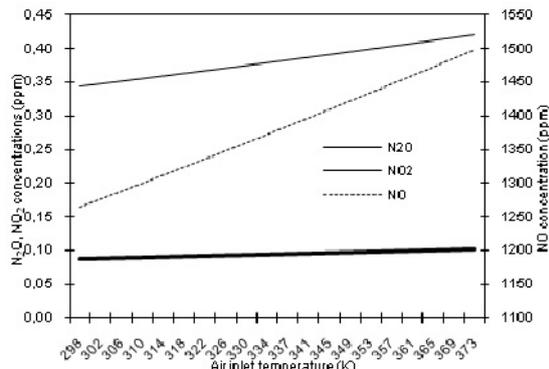higher temperature is possible to initiate the thermal NO_x reactions.

Figure 7. NO_x and N_2O emissions as function of air inlet temperature in co-combustion

6. Conclusions

NO_x reduction reaction at higher temperature in single coal combustion can be initiated by oxygen and soot. In co-combustion, NO_x reduction may also be supported by biomass reductive radicals' reactions, in addition to oxygen and soot reactions.

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