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A REBURN MODEL FOR PREDICTION NO_X AND Hg CAPTURE WITH COAL AND FEEDLOT BIOMASS (CATTLE MANURE) AS REBURN FUELS

Task 4: Model Development

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ABSTRACT

About 110 million tons of dry animal manure (feedlot biomass, FB) is produced annually in the United States, which presents a difficult disposal problem in many watersheds and airsheds. A possible solution is to develop an animal waste utilization technology through co-firing, use as a reburn fuel, and gasification. The reburn process is a technology by which the NOx formed by the coal fired in main burners of the power plants is reduced to harmless N_2 using a set of additional burners firing a variety of fuels (coal, methane, natural gas or liquid hydrocarbons; about 10-15 % of total heat), called reburn fuel, down stream from the lean primary zone (PZ) to create a fuel rich reburn zone where NO_x is reduced through reactions with hydrocarbons (reverse prompt NOx). After the reburn zone (RZ) , additional air is injected in the burnout zone to complete the combustion process. Typically 60 % reduction is achieved with natural gas as reburn fuel. Experiments performed with FB as reburn fuel resulted in capture of NO_x as high as 90 % . The present task deals with development of a reburn model to predict the NO_X emission when coal (Wyoming Sub-bituminous and Texas Lignite) , FB and coal:FB blends are used as reburn fuels and to elucidate the mechanisms governing the reduction process. An additional feature is the development of a model for Hg release and oxidation in gas phase to $HgCl^2$. The events of reburn jet are traced using Lagrangian frame of reference with respect to an observer traveling with the gas from the reburner; the hot gases from the main burner mixes with the reburn gas and particle stream with gradual increase in temperature and change in composition of gases surrounding the particles as gas phase and heterogeneous reactions proceed. The reburn solid fuel particles are grouped into five particle size groups with each group described by a mean diameter. Composition of the gas phase in the free stream (CH_4, CO, CO_2, H_2, HCN, H_2O, N_2, NH_3, NO, O_2) and at the particle surface, temperatures for the reburn gas and for each particle size group, total mass, fixed carbon mass, diameter and density of each class of particle, volatile matter (VM), products of reaction, fuel bound nitrogen (FBN) pyrolysis and Hg evolution rate and species left in the solid fuel are tracked. For the mercury, the extra species tracked are: Cl, Cl2, HCl, Hg, HgCl, HgCl2, and OH. The model yields poor capture of NO_x by coal and significant capture by FB and the predictions agree well with the data from experiments. The model also confirmed that vitiated air can be effectively used in the reburner to achieve even lower NOx emissions. With coal as a reburn fuel, the Hg oxidation fraction of mercury is about 30% while for the feedlot biomass, it is above 90%. Further an isolated single particle model has been developed predicts that the mercury oxidation is also a function of the gas temperature within the boundary layer surrounding the partice and the diameter of particle. Also the single particle model predicts a significant increase of the oxidized mercury using blends of coal and biomass.

1. INTRODUCTION

The reburn process is a technology by which the NO_x formed by the main burners of the power plants is reduced to harmless N_2 using a set of additional burners firing a variety of fuels (coal, methane, natural gas or liquid hydrocarbons; about 10-15 % of total heat), called reburn fuel, down stream from the lean primary combustion zone to create a fuel rich reburn zone where NO_x is reduced through reactions with hydrocarbons (reverse prompt NO_x). The nitrogen compounds recombine with oxygen to form NO_x, or combine with NO to form N_2. The extent of reduction of NO_x is a function of the operating parameters used in the reburn process and properties of the reburn fuel. After the reburn zone, additional air is injected in the burnout zone to complete the combustion process. Typically 60 % reduction is achieved with natural gas as reburn fuel. A diagram of the entire process with the different combustion zones is shown in Figure 1. This process is somewhat similar to air staging where the fuel is first burnt in a rich primary zone to minimize the production of NO_x, and later overfire air is injected to complete the combustion process. Primary zone (PZ) is the zone where main fuel is burnt with slightly excess air where NO_x is produced. Reburn zone (RZ) is the zone into which reburn fuel is supplied with deficient air so that the reburn air after mixing with main product gases produces the desired equivalence ratio. The use of animal waste as a reburn fuel resulted in a reduction of NO_x over 80%, better than with conventional fuels, and close to the results typically obtained through advanced reburning [Annamalai and Sweeten 2005a;

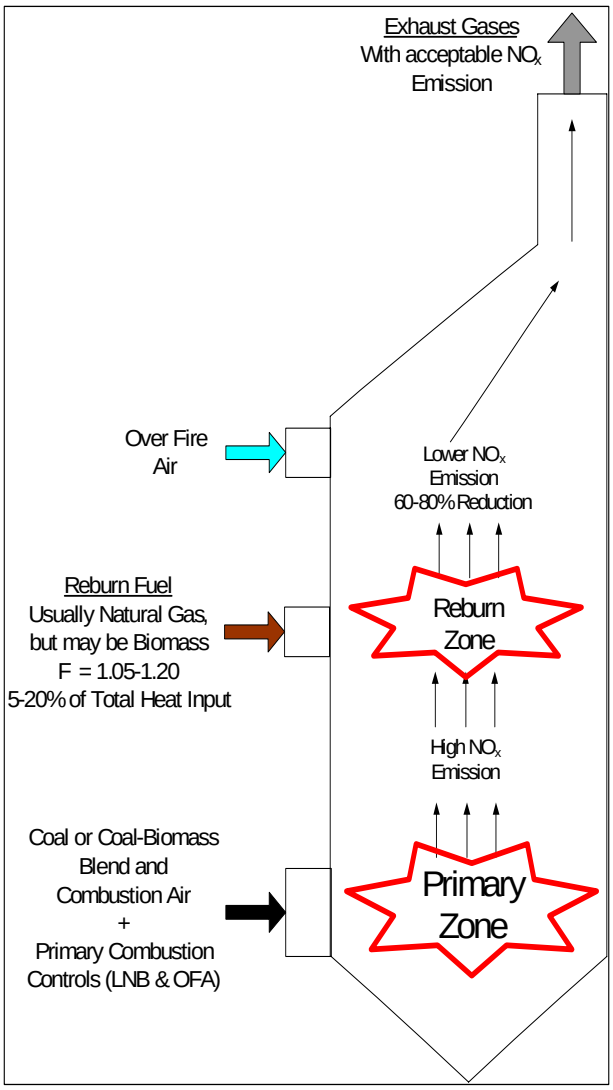

Figure 1. Typical Reburn Process in Boilers

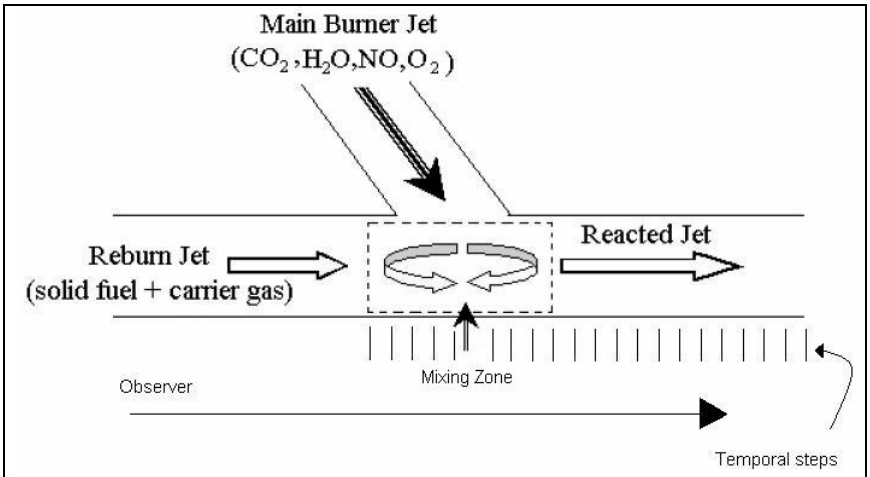

Figure 2. Schematic of Reburn Model

Annamalai et al 2005b; Thien and Annamalai, 2001]. Goal of this task is to develop a model to predict the NO_x reduction and to elucidate the mechanisms governing this process.

2. EXPERIMENT

The experimental setup is described elsewhere [Annamalai et al, 2006]. In a real boiler NO_x is produced along with hot gases by burning coal. In a laboratory set up, the NO_x production is simulated by burning NH_3 and hot gases is produced by burning natural gas. The small scale experimental facility is composed of a main burner fired by natural gas (almost methane) which provides 70% of the total thermal power. The main flame is doped with ammonia in order to create a known amount of NO in the main burner gases; the temperature, oxygen concentration and NO_x in ppm of the gases are kept constant for all the experiments. The reburn fuel with air or a vitiated gas mixture (reduced O_2 %) is then injected into this main gas stream. The NO is then measured in ppm at exit of the burner and % reduction is estimated. Along with NO measurements, attempts were made to measure Hg and oxidized $HgCl_2$.

3. REBURN MODEL

In this section, a brief overview of model is given. More details of modeling are given elsewhere [Colmegna, 2006]. The model is described by the schematic shown in Figure 2. The total mass leaving the main burner is the sum of the mass flow of ammonia (i.e. products of combustion to NO and H_2O), air and fuel supplied. The composition of the products is known, so also the mass flow rate of every species is known. The events are traced using Lagrangian frame of reference with respect to an observer traveling with the gas from the reburner, and observes the mass to be increasing as the flow from the main burner mixes with the reburn gas and particle stream with gradual increase in temperature and change in composition of gases surrounding the particles. The reburn solid particles are grouped into various size groups. The particles heat up; pyrolyze releasing species k (e.g. CH_4, CO etc) which undergoes gas phase reactions producing CO_2, H_2O, NO etc. Composition of the gas phase in the free stream (CH_4, CO, CO_2, H_2, HCN, H_2O, N_2, NH_3, NO, O_2) and at the particle surface, temperatures for the reburn gas and for each particle size group, total mass, fixed carbon mass, diameter and density of each class of particle, volatile matter (VM), products of reaction, fuel bound nitrogen (FBN) pyrolysis rate, Hg evolution rate and species left in the solid fuel are tracked. For the mercury, the extra species tracked are: Cl, Cl_2, HCl, Hg, HgCl, $HgCl_2$, and OH. The Hg undergoes oxidation in gas phase to $HgCl_2$. Since the extent of oxidation for Hg with coal: feedlot biomass blend is required, two different types of fuel are included for the solid fuel particles. The size distribution for each solid fuel has been measured for all the fuels used in the experimentation [Goughnour, 2006 b]. For all the simulations the

reburn fuel is solid fuel represented by five particle size groups (j=1..5). For the purpose of the modeling, each group is described with a mean diameter.

3.1 Assumptions

3.1.1 Main burner

- The main burner fuel is methane
- The A:F ratio of main burner is prescribed
- Combustion for the main burner fuel is assumed to be complete to water and CO_2
- The NO_x at the exit of the main burner is generated only by ammonia. The amount of ammonia will depend only on the amount of NO desired.
- Thermal NO_x is ignored. The conversion of ammonia to NO will be considered complete (no ammonia present in the exhaust of the main burner)
- The temperature of the gases leaving the main burner zone is known from experimental data
- The thermal heat input from the main burner is fixed (70000 BTU/hr)
- The process is assumed to take place at atmospheric pressure.

3.1.2 Reburner

- Reburn fuel consists of known size distribution
- The ash percentage is assumed to be evenly distributed in all the particle sizes
- The mixing process is assumed to be isenthalpic.
- The OH is assumed to exist at local equilibrium concentration
- The Hg and N species are assumed to be in trace amounts.
- For all the simulations the reburn fuel is solid fuel represented by five particle size groups.
- All the properties and kinetics of the solid fuel are assumed to be independent of the particle size.
- The particles are spherical.
- Moisture from the reburn solid fuel is assumed to evaporate instantaneously when the fuel is injected
- Ash is assumed to be inert.
- The volatiles release follows a single step global reaction kinetics model with activation energy of E_{pyro} and pre exponential factor A_{pyro}.
- Pyrolysis occurs volumetrically
- The activation energy E_{pyro} and the pre exponential factor A_{pyro} are different for coal and for biomass.
- The composition of the pyrolysis gas is considered to be constant throughout the pyrolysis process.
- The fuel N pyrolysis yields NH_3, HCN, N_2 and the proportion among the N compounds in the products is assumed to be known from the literature but subject to N atom balance.

- In the cases where no reaction rates have been found for biomass chars, the heterogeneous carbon reactions have been assumed to be the same as that for lignite char , as low rank coals are the closest to the biomass as combustion characteristics
- Heterogeneous carbon reactions occur at constant density
- A quasi-steady state behavior exists for the particle.
- The particles have a uniform temperature.
- All processes occur at constant pressure.
- Chlorine is released from the reburn fuel as Cl_2 and HCl.

3.2 Main Burner modeling

As the power coming from the main burner is fixed (70000 BTU/hr, based of the HHV of the fuel), it is possible to compute the mass flow of the main burner fuel:

$$m_{fuel\,MB} = \frac{Power_{MB}}{HHV_{fuel\,MB}} \tag{1}$$

The main burner fuel is assumed as gaseous $CH_xO_yN_z$ (g)

$$\begin{aligned} &CH_xO_yN_z + w\cdot NH_3 + \left(1+\frac{a}{100}\right)\cdot\left(1+\frac{x}{4}+\frac{y}{2}\right)\cdot\left(O_2+3.76\cdot N_2\right) \rightarrow CO_2 + \left(\frac{x}{2}+\frac{3\cdot w}{2}\right)\cdot H_2O \\ &+\left(\frac{a}{100}\cdot\left(1+\frac{x}{4}-\frac{y}{2}\right)-\frac{5\cdot w}{4}\right)\cdot O_2 + w\cdot NO + \left[\frac{z}{2}+3.76\cdot\left(1+\frac{a}{100}\right)\cdot\left(1+\frac{x}{4}-\frac{y}{2}\right)\right]\cdot N_2 \end{aligned} \tag{2}$$

With known excess air % and specified NO in ppm (dry), one can solve for a and w and the composition of products including O_2 % with stated assumptions.

3.3 <u>Reburn modeling</u>

The reburn fuel is known in the generic form as $CH_{x1}O_{y1}N_{z1}$ (s). Fixed carbon will be consumed with the heterogeneous reactions at the particle surface; in the case of blends there will be two different solid fuels, each one with its own empirical formula. For the general case of a blend, considering y_{coal} and y_{FB} as the mass fraction of the two solid fuels, the amount of reburn firing rate is estimated as:

$$\begin{aligned} \dot{m}_{fuel\,RB} &= \frac{Power_{RB}}{HV_{fuel\,FB}\cdot y_{FB} + HV_{fuel\,coal}\cdot y_{coal}} \\ \dot{m}_{FB} &= \dot{m}_{fuel\,RB}\cdot y_{FB} \\ \dot{m}_{caol} &= \dot{m}_{fuel\,RB}\cdot y_{coal} \end{aligned} \tag{3}$$

If ν_{O2} is the stoichiometric oxygen to fuel ratio (mass basis) for a generic fuel $CH_{x1}O_{y1}N_{z1}$ and the reburn zone equivalence ratio is ϕ_{RZ}, then the required flow rate of oxygen and carrier gas are given as

$$\dot{m}_{O2,RZ} = \frac{\dot{m}_{coal,DAF} \cdot \nu_{O2,coal} + \dot{m}_{FB,DAF} \cdot \nu_{O2,FB}}{\Phi_{RZ}} - \dot{m}_{O2,MB} \tag{4}$$

$$\dot{m}_{carrier\,gas,RB} = \frac{\dot{m}_{O2,RZ}}{Y_{O2,RZ}} \tag{5}$$

Where $Y_{O2,RZ}$ is the oxygen mass fraction in the reburn carrier gas. In the case of pure air $Y_{O2,RZ}$ = 0.23 while for vitiated air, $Y_{O2,RB} < 0.23$.

3.3.1 Pyrolysis Model

It is assumed that the volatile loss occurs volumetrically, as during pyrolysis the gases leaving will leave a kind of spongy structure, without altering the external dimension. Thus density will change with time. Fuel pyrolysis is described by a finite kinetics (Badzioch S. et al., 1970, Raman et al., 1981) and it depends on the type of fuel. The exact composition of the pyrolysis gas is determined using the atom conservation and the data from the proximate analysis which specifies the fraction of volatiles and fixed carbon in the fuel, assuming that no oxygen or hydrogen will be left in the particle after the pyrolysis [Østberg et al., 1998].

a) Volatile matter release: For a single step global reaction kinetics model,

$$\left.\frac{dm_{pyro}}{dt}\right|_j = A_{pyro} \cdot VM_{remain,j} \cdot \exp\left(\frac{-E_{pyro}}{R \cdot T_{p,j}}\right) \qquad \left[\frac{kg_{VM}}{s}\right] \tag{6}$$

$VM_{remain,j}$ represents the mass of volatiles left in the j-th particle class. The VM is assumed to mix instantaneously with the free stream at each temporal step. Note that T_p stands for particle temperature, so each size group has its own temperature with different rates of release of VM.

b) FBN pyrolysis rate: the two most widely used methods are : i) FBN pyrolysis rate proportional to the pyrolysis rate and ii) FBN pyrolysis rate following its specific kinetics.

For the first case, the FBN release rate is given as:

$$\left.\frac{dm_{FBN,pyro}}{dt}\right|_j = \left.\frac{dm_{pyro}}{dt}\right|_j \cdot \frac{N_{initial}}{VM_{initial}} \qquad \left[\frac{kg_N}{s}\right] \tag{7}$$

where $\left.\frac{dm_{pyro}}{dt}\right|_j$ is the pyrolysis rate.

For the second case the FBN emission is described with a single reaction model [Pohl, 1977]:

$$\left.\frac{dm_{N-pyro}}{dt}\right|_j = A_{FBN} \cdot N_{remain,j} \cdot \exp\left(\frac{-E_{FBN}}{R \cdot T_{p,j}}\right) \qquad \left[\frac{kg_N}{s}\right] \tag{8}$$

3.3.2 Heterogeneous Recations

As the pyrolysis proceeds, the carbon in solid fuel can undergo heterogeneous reactions if pyrolysis rates are slow; once pyrolysis is complete, only char reactions proceed. The reactions included in the model are: the reaction of fixed carbon (char) with oxygen to produce CO or CO_2; with H_2O (steam) to produce CO and H_2; with CO_2 to CO etc, and Char N with O_2 to NO and with NO to N_2.

C(s) + 1/2 O2 → CO, $h_{c,I}$= 9203 kJ/kg of C (I-h)

C(s) + O2 → CO2 $h_{c,II}$ = 32766 kJ/kg of C (II-h)

C(s) + CO2 →2 CO $h_{c,III}$ = -14360 kJ/kg of C (III-h)

C(s) + H2O(g) → CO + H2 $h_{c,IV}$ =- 10932 kJ/kg of C, (IV-h)

C(s) + NO → CO + 0.5 N2 $h_{c,V}$ = -16736 kJ/kg of C (V-h)

N(s) + 0.5 O2 → NO $h_{c,V}$ = 6428 kJ/kg of C (VI-h)

The FC consumption rate for each of the reaction *i*, for the particle size *j* can be computed as:

$$\dot{m}_{C,i,j} = \rho_{w,j} \cdot k_{C,i,j} \cdot Y_{react\,i,,jw} \cdot \pi \cdot d_{p,j}^2 \qquad \left[\frac{kg}{s}\right]_{per\ particle} \tag{9}$$

Knowing the fixed carbon consumption rate and the stoichiometry of the heterogeneous reactions it is possible to compute the contributions of the gas phase components:

$$\dot{m}_{k,hetero} = \sum_{j=1}^{n\,class}\left[\sum_{i=1}^{hetero\,react}\left(\upsilon_{i,k}\cdot\dot{m}_{C,i,j}\right)\cdot N_{particles,j}\right]\cdot\frac{M_k}{M_C}\quad\left[\frac{kg}{s}\right] \tag{10}$$

where υ is the stoichiometric coefficient on mass basis (e.g. for reaction II, υ_{O2} = 2.667 kg of oxygen per kg of C). In case of blends the summation must be added over the two fuels. The density of the gas phase must be computed at the surface of the particle and also the mass concentration of the reactants must be computed in the boundary layer surrounding the particle.

3.3.3 Particle density, diameter (d_p) and mass (m)

$$(\pi d_p^{\,3}/6)\frac{d\rho}{dt} = -\left.\frac{dm_{pyro}}{dt}\right|_{j\,remain} \tag{11}$$

The diameter of the particle shrinks as carbon burns:

$$\left.\frac{d(d_p)}{dt}\right|_j = -\frac{2\cdot\dot{m}_{C,j}}{\pi\cdot\rho_{p,j}\cdot d_{p,j}^2} \tag{12}$$

$$\dot{m}_{p,j} = \dot{m}_{C,j} + \frac{\dot{m}_{VM,j}}{N_{particles,j}} + \frac{\dot{m}_{FBN,j}}{N_{particles,j}}\quad (mass\ loss\ from\ each\ particle\ of\ class\ j) \tag{13}$$

where m_C refers to the carbon consumption rate of a single particle. It is also possible to compute the mass of each particle at the next temporal step. For the general class *j*, the formula will be:

$$m_{particle,j,t+1} = m_{particle,j,t} - \left(\dot{m}_{C,j} + \frac{\dot{m}_{VM,j}}{N_{particles,j}} + \frac{\dot{m}_{FBN,j}}{N_{particles,j}}\right)\cdot dt \tag{14}$$

3.3.4 Energy conservation for the Particles

The particles exchange heat with the gas phase through convection and radiation. The oxidation reactions of the char are exothermic and so tend to heat up the particle, while the gasification reactions require heat to proceed and tend to cool down the particle. Also the release of the volatiles needs some energy to proceed and so tends to cool down the particle; however the last contribution is not very significant.

3.3.5 Homogeneous Reactions

These are the reactions that take place in the gas phase; for these reactions the species concentrations are directly computed knowing the composition of the gas phase stream.
Oxidation Reactions: three reactions will be used to consider the oxidation of hydrogen, methane and CO. The reactions produce CO_2 and H_2O volumetrically ($\dot{w}_k$).
NO reactions: four reactions are used to describe the NO evolution: two reactions for the reaction of ammonia that destroy or produce NO, and the other two concern the reaction of HCN to destroy or produce NO.

From the stoichiometry of the each reaction it is possible to compute the moles of species k added to /destroyed in gas phase:

$$\dot{n}_{\mathrm{hom}\,o,k} = \sum_{i=1}^{7} \upsilon_{i,k} \cdot w_i \cdot \frac{R_{kg} \cdot m_{TOT,gas} \cdot T_g}{p} \left[\frac{kmol}{s}\right] \qquad (15)$$

Where w_j is the reaction rate for a general reaction j, $\upsilon_{k,j}$ is the stoichiometric coefficient of species k in reaction *j*, and it is positive if the species is being produced and negative if the species k is being consumed. Knowing the molar mass of each species it is possible to compute the rate of addition or consumption of species k.

$$\dot{m}_{\mathrm{hom}\,o,k} = \sum_{i=1}^{7} \dot{n}_i \cdot M_k \qquad \left[\frac{kg}{s}\right] \qquad (16)$$

3.3.6 Mixing model

For the mixing process an exponential model is used to simulate the mixing of reburn gases with the main burner gas and reburner gas. With respect to an observer traveling with the reburn mass, the total mass is composed of the reburn mass and a fraction of the main burner mass that is added gradually over time; eventually the sum approaches a total mass equal to the sum of reburn mass and main burner gasses as time tends to infinity.

$$\dot{m}_{RB,t} = \dot{m}_{RB,t=0} + \dot{m}_{prod,MB} \cdot \left(1 - \exp\left(-\frac{t}{\tau_{mix}}\right)\right) \qquad (1714)$$

τ_{mix} is the mixing time constant. The mixing time constant is estimated from experiments to be around 40 ms [Annamalai et al 2006]. The amount of mass from the main burner added over a period of time dt:

$$d\dot{m}_{MB} = \frac{\dot{m}_{prod,MB}}{\tau_{mix}} \cdot \exp\left(-\frac{t}{\tau_{mix}}\right) \cdot dt \tag{18}$$

3.3.7 Energy conservation for the gas phase

In the gas phase, it is necessary to take in consideration the mixing of the mass from the main burner. The gas receives the convective and radiation heat from the particle, addition of enthalpy due to the gas stream originating from the particle, chemical heat due to gas phase oxidation reactions and enthalpy from main burner gases due to mixing. Thus the gas phase energy conservation yields gas temperature.

3.3.8 Mercury and Chlorine modeling

Mercury is released from the reburn fuel in the elemental form, while chlorine is released as Cl_2 and HCl. The repartition of chlorine between Cl_2 and HCl is 0.1 and 0.9, mass fractions, assumed from literature. The Hg and the chlorine are assumed to be released with the volatiles. The path toward the oxidation of mercury to $HgCl_2$ will be described by the following reactions: [Xu *et al*,. 2003].

$$\begin{aligned}
&1: HCl + OH \rightarrow H_2O + Cl && k = 2.71 \cdot 10^{7} \cdot T^{1.65} \cdot \exp\left(\frac{937}{T}\right) \left[\frac{kmol}{m^3 \cdot s}\right] \\
&2: Hg + Cl + M \rightarrow HgCl + M && k = 2.4 \cdot 10^{8} \cdot T^{1.4} \cdot \exp\left(\frac{7500}{T}\right) \left[\frac{kmol}{m^3 \cdot s}\right] \\
&3: HgCl + Cl + M \rightarrow HgCl_2 + M && k = 2.19 \cdot 10^{18} \cdot \exp\left(\frac{-1614}{T}\right) \left[\frac{kmol}{m^3 \cdot s}\right]
\end{aligned} \tag{19}$$

The OH is assumed to come from the dissociation of water according to the following equilibrium reaction:

$$H_2O \Leftrightarrow OH + \frac{1}{2} \cdot H_2 \tag{20}$$

More details of reaction are given elsewhere [Colmegna, 2006]. As these species are as trace amounts, they will not alter the overall energy and mass conservation in the gas phase.

4. ISOLATED PARTICLE MODEL

The current reburn model does not consider the effects of boundary layer on the pollutant formation and destruction. For e.g., there exist temperature and species concentration variation around the particle. In order to understand the effects of boundary layer on extent of Hg oxidation,

a more fundamental isolated particle model has been also developed. A simple description of the model is given in Appendix. More details are given elsewhere [Puchakayala, 2006].

5. RESULTS AND DISCUSSION

5.1 Computer Code and Input and Output Data

A computer code has been developed based on above model description. The input of the code is:

- Main burner: thermal rating, fuel characteristics, excess air, inlet temperature and initial NO_x.
- Reburner: thermal rating, equivalence ratio in the reburn zone, inlet temperature and composition of the reburn gas.
- Solid Reburn Fuel: proximate and ultimate analyses, size distribution (mass %, dia), density, specific heat, heating values, pyrolysis kinetics parameters, FBN products composition and Hg and Cl concentration in fuel.

The outputs vs. time are:

- Temperature for the reburn gas and for each particle diameter.
- Composition of the gas phase in the free stream and at the particle surface.
- Total mass, fixed carbon mass, diameter and density of each class of particles.
- VM and FBN pyrolysis rate and species left in the fuel.
- Concentration of NO.
- Hg and $HgCl_2$.

The data input for the code are given in Tables 1 to 5.

Table 1: input data for the main burner

$X_{O2, RB}$ = 0.125 (volume fraction) [Annamalai et al, 2006].

Fuel	Methane (CH_4)
Total Power	30kw (100000 Btu/hr)
Main burner power	21kw (71655 Btu/hr)
hHV methane	57100kJ/kg
% Excess air MB	5
NO simulated from MB	400ppm
Inlet temperature of air and fuel	300K

Table 2: General data for the Reburner

Fuel	Coal, FB or Coal – FB blends
Reburner power	9kw (28345 Btu/hr)
Equivalence ratio considered	1 to 1.15
Inlet temperature	300K (80.33F)

Mixing time	35ms

Table 3: Solid Fuel Properties

Property		LAPC	HAPC	TXL	WYO
Proximate analysis	Moisture	19.64	17	38.34	32.88
	Ash	16.5	53.85	11.46	5.64
	FC	11.54	3.36	25.41	32.99
	VM	52.33	25.79	24.79	28.49
Ultimate analysis (DAF)	C	52.92	51.19	74.06	75.67
	H	5.72	4.782	4.22	4.44
	O	37.47	39.09	19.14	18.36
	N	3.087	3.863	1.35	1.074
Cl content [kg Cl / kg of fuel]		0.727	0.281	0.013	0.01
Hg content [mg Hg / kg of ash]		0.04	0.03	0.01	0.01
LHV as received [kJ/kg]		13283	5214	14306	18219
Density [kg/m3]		1100	1100	1300	1300
Pyrolysis kinetics	A [1/s] **	$6.79\ 10^{9}$	$6.79\ 10^{9}$	$1.67\ 10^{13}$	$1.67\ 10^{13}$
	B [kJ/kmol] **	140000	140000	223000	223000
Heat of Pyrolysis of VM [kJ/kg]		-400	-400	-400	-400
Specific heat [kJ/kg K]		1.1	1.1	1.1	1.1
FBN distribution N_2:NH_3:HCN +		1:6:3	1:6:3	0.1:1.2:8.7	0.01:1.61:8.28

** for feedlot biomass: Brown, 2001
For coal: Suuberg, 1978
\+ for feed lot biomass: Sami, 2000
For TXL and WYO: Kambara, 1993

Table 4: Particle size distribution

Particle size distribution				
Mean Diameter [mm]	HAPC [%]	LAPC [%]	TXL [%]	WYO [%]
1596	0.01	0.05	0.01	0
1015	0.03	0.1	0.00	0
570	1.68	7.58	4.97	1.68
225	6.44	27.21	33.72	15.35
113	13.73	22.56	37.09	45.01
60	20.43	16.06	11.82	21.75
22.5	57.69	26.44	12.38	16.18
SMD [mm]	32.71	56.28	81.02	64.44

Table 5: Mercury and Cl content

Mercury and chlorine content			
	LAPC	TXL	WYO
Hg [mg/kg as received basis]	0.06	0.17	0.14
Cl [% in ultimate analysis]	0.831	0.004	0.007

5.2 NO_x

5.2.1 Pure air as Carrier gas

All the results for the different reburn fuels at ER = 1, with lateral injection, are compared with the prediction (Figure 3).

In most cases the prediction from the model agrees with the data from experiments. It is observed that the reduction using feedlot biomass as a reburn fuel is significant. If one uses Texas Lignite or Wyoming coal as reburn fuels, NO concentration is much higher. The results for the blends of Texas Lignite and feedlot biomass fall between the results of two pure fuels.

5.2.2 Vitiated air as Carrier Gas

Results are shown in Figure 4. It is seen that the NO concentration is further reduced at the exit of

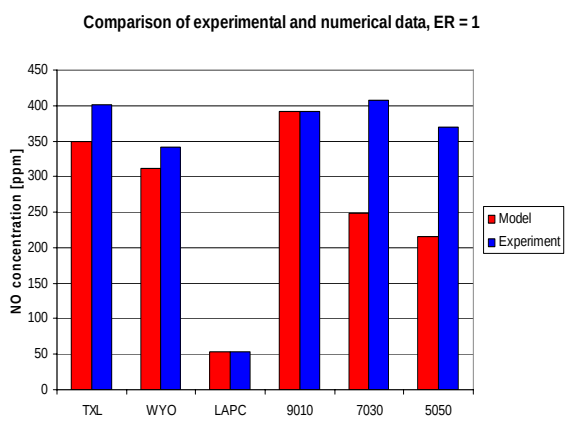

Figure 3. Comparison of NO results, ER = 1; lateral Injection

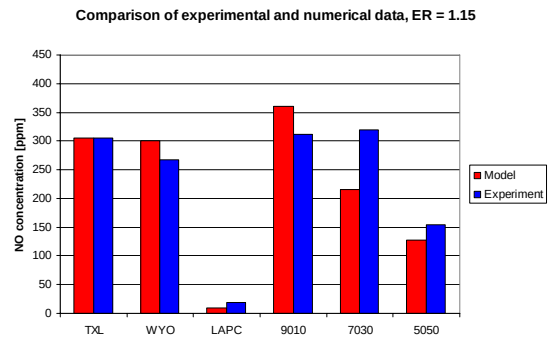

Figure 4. Comparison of NO results, ER = 1; lateral Injection; vitiated air

the furnace. The results from the simulation are still reasonably in close agreement with the ones from the experiments. Also in this case, feedlot biomass achieves the best NO_x reduction.

5.3 Hg

In this case there are no experimental data available in order to compare the results. In the case of mercury it is important to determine % converted into $HgCl_2$ which is much easier to remove from the gas flow with conventional wet scrubber technologies. Both the Texas Lignite and the Wyoming coal have less than 30% of oxidized mercury, while biomass has over 90% of the

mercury oxidized. It is interesting to note that even using blends of biomass and coal the amount of oxidized mercury is still over 90%. (Figure 5)

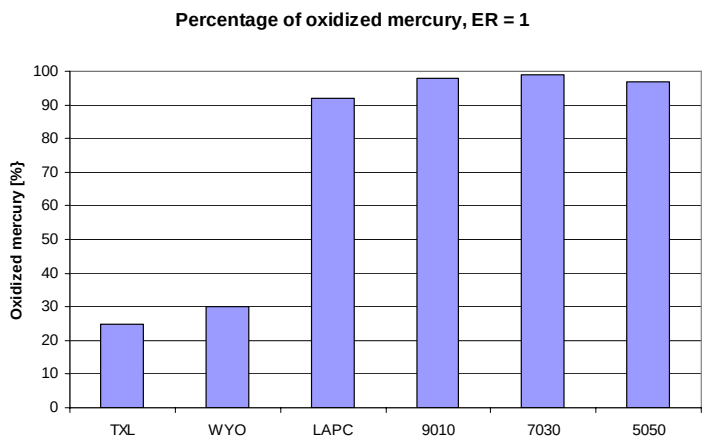

Figure 5. Mercury oxidation Model Results for ER = 1; lateral Injection; Pure air, Different Fuels

6. ISOLATED PARTICLE MODEL RESULTS

In order to quantitatively ascertain the effects of boundary layer, data was generated using isolated particle model.

In this model the mercury oxidation is studied as a function of the temperature of the gas around the particle and as a function of the particle size.

Figure 6 shows that as the temperature of the gas surrounding the particle increases the amount of mercury oxidized decreases. The decrease is particularly steep as temperature goes over 1650K.

Table 6: influence of particle diameter on Hg oxidation

Diameter (μm)	% Hg oxidized
24	0.5
46	1.0
70	4.0
100	11.0
150	18.0
200	24.0

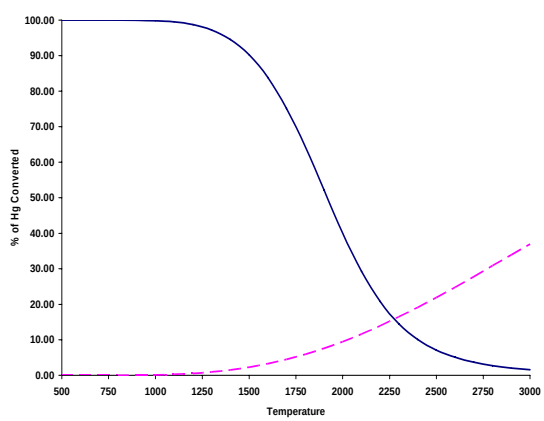

Figure 6. Equilibrium mercury speciation in flue gas as function of temperature. (Initial moles of Hg: 1.6E-08, Cl_2 :1E-04). Blue: $HgCl_2$; Pink: HgCl

Table 6 shows that the amount of mercury oxidized is also a function of the particle diameter: as the diameter increases the percentage increases.

Table 7: effect of blending on Hg oxidation

	% Hg oxidized
Texas Lignite -100%	11
Texas Lignite-biomass – 90:10	65
Texas Lignite-biomass – 80:20	87

From Table 7 it is also possible to see that as coal

is mixed with biomass the amount of oxidized mercury increases significantly.

7. CONCLUSIONS

1. A model has been developed to predict the NO_x reduction using different solid fuels as reburn fuels and to predict the evolution of mercury from the fuel.
2. The results concerning the NO_x reduction matches well with the data from experiments.
3. This model also confirmed that vitiated air can be effectively used in the reburner to achieve lower NO_x emissions.
4. Texas Lignite and Wyoming coal have shown similar performances at the reburner with low NO reductions; the blends yield results between those of pure coal and pure feedlot biomass.
5. With coal as a reburn fuel, the Hg oxidation fraction of mercury is about 30% while for the feedlot biomass, it is above 90%.
6. The single particle model that has been developed predicts that the mercury oxidation is also a function of the gas temperature and of the particle diameter.
7. Also the single particle model predicts a significant increase of the oxidized mercury using blends of coal and biomass.

8. REFERENCES

Annamalai, K. , Goughnour P. G., Hyukjin, O., Uday, A., and Sweeten J, 2006, "NO_x Reduction with the Use of Feedlot Biomass as a Reburn Fuel", Task 2 Report submitted to TCEQ,Austin, TX

Annamalai, K and Puri, I, Combustion Science and Engineering, Taylor & Francis (2006) under proof reading

Annamalai, K. and J.M. Sweeten. 2005a. Reburn System with Feedlot Biomass. US Patent No. US 6,973,883 B 1. U.S. Patent & Trademark Office, Washington, DC, 20231. 12 p. Date of Issue: December 13, 2005.

Annamalai, K., J.M. Sweeten, S. Mukhtar, S. Arumugam, S. Priyadarsan. 2005b. A Novel Application of Feedlot Manure as Reburn Fuel for NOx Reduction in Existing Coal-Fired Plants. Final Report, Grant No. 93-36200-870-, National Center for Manure & Animal Waste Management, North Carolina State University, Raleigh, NC. January 31. 61p.

Badzioch S. and Hawksley P. G. W., 1970, "Kinetics of Thermal Decomposition of Pulverized Coal Particles", Ind. Eng. Chem. Pro. Design Dev., Vol. 9, pp/ 521-530

Brown A. L., Dayton D. C., Nimlos M. R. and Daily J. W., 2001, "Design and Characterization of an Entrained Flow Reactor for the Study of Biomass Pyrolysis Chemistry at High Heating Rates", Energy & Fuels, Vol. 15, pp. 1276-1285

Colmegna G, 2006, "Reburn Modeling to predict NOx capture by Biomass Fuels" MS Thesis (under preparation), Texas A&M University

Du Xiangyang and Kalyan Annamalai, Combustion and Flame, 97(1994) 339-354

Goughnour P. G., 2006 b, "NO_x Reduction with the Use of Feedlot Biomass as a Reburn Fuel", MS thesis, Texas A&M University

Kambara Shinji, Takarada Takayuki, Yamamoto Yasuhiro and Kato Kunio, 1993, "Relation between Functional Forms of Coal Nitrogen and Formation of NOx Precursors during Rapid Pyrolysis", Energy and Fuels 7 pp. 1013-1020

Østberg M., Glarborg P., Jensen A., Johnson J. E., Pedersen L. S. and Dam-Johansen K., 1998, "A Model of the Coal Reburning Process", 27th Symposium (International) on Combustion, The Combustion Institute, pp. 3027-3035

Pohl J. H., Sarofim A. F., 1977, "Devolatilization and Oxidation of Coal Nitrogen", 16th Symposium (International) on Combustion, The Combustion Institute

Puchayakala, M. , 2006, "Mercury Emission Behavior During Isolated Particle Combustion, " PhD Thesis, Mech. Engineering, Texas A&M University (in preparation)

Raman P., Walawender W. P., Fan L. T. and Howell J. A., 1981, "Thermogravimetric Analysis of Biomass. Devolatilization Studies on Feedlot Manure", Ind. Eng. Chem. Process Des. Dev., Vol. 20, pp. 630-636

Roesler J.F., R. A. Yetter, F.L. Dryer. Combustion and Flame, 100 (1995) 495–504

Sami, M., 2000, "Numerical Modeling Of Coal-Feedlot Biomass Blend And NOx Emission In Swirl Burner", PhD Thesis, Texas A&M University

Suuberg E. M., Peters W. A. and Howard J. B., 1978, "Product Composition and Kinetics of Lignite Pyrolysis", Ind. Eng. Chem.Process Des. Dev, Vol. 17 (1) pp. 37-46

Thien, B. and Annamalai , K, 2001, " Reduction of NO Through Reburning With Coal and Feedlot Biomass" , National Combustion Conference, Oakland, Ca. March 25-27

Shao Dakang, Erik J. Hutchinson, Haibin Cao, and Wei-Ping Pan, Energy & Fuels,8,(1994)399-401

Xu M., Qiao Y., Zheng C., Li L and Liu J., "Modeling of homogeneous mercury speciation using detailed chemical kinetics", 2003, Combustion and Flames, Vol. 132, pp. 208-218

Widmer N.C., J. West. Thermochemical Study of Mercury Oxidation in Utility Boiler Fuel Gases, 93rd Annual Meeting, Air & Waste Management Association, Salt Lake City, Utah, 2000

APPENDIX A: DESCRIPTION OF THE SINGLE PARTICLE MODEL

OBJECTIVE

The objective of this work is to model the mercury evolution and oxidation for a single coal particle and to determine the extent of Hg oxidation under combustion conditions of coal particle.

EQUILIBRIUM STUDIES

Distribution of mercury species in coal combustion flue gases has been calculated using equilibrium reactions. The calculations demonstrated that the gas phase equilibrium for mercury-containing species in coal-fired power plant exhaust is not valid at temperatures below 800^0K. The most important for the oxidation of mercury in the post-combustion gases is the chlorine-contained species. The calculations are done for two different equilibrium reactions.

$Hg + Cl_2$ ----> $HgCl_2$
$Hg + Cl_2$ ----> $HgCl + Cl$

The results show that all of the Hg exists in the form $HgCl_2$ below 750^0K. From the equilibrium studies, HgCl is more dominant than $HgCl_2$ at higher temperatures. The amount of Hg oxidized between the above temperatures depends on the amount of chlorine present in the coal. Mercury content of the coal has no control on the distribution of mercury species. It is noted that equilibrium is not be attained in flue gas due to fact that flue gas cools rapidly as heat is transferred from water to steam and kinetic time scale is longer due to lower temperature.

ISOLATE COAL PARTICLE

A transient model developed previously by [Du and Annamalai] is modified to include the mercury and chlorine chemistry. The following is an illustration for an isolated particle pyrolysis and combustion of coal particle.

Consider a cold coal particle of radius *a* suddenly placed in a hot gas containing oxygen (Fig A1). The thermal wave propagates from the ambience into the coal particle. When the temperature of the coal particle reaches the pyrolysis level, thermal decomposition of the coal occurs and releases volatiles that diffuse into the surrounding atmosphere. The composition and quantity of the volatile matter will vary with the rate of heating, the time of heating and the temperature reached.

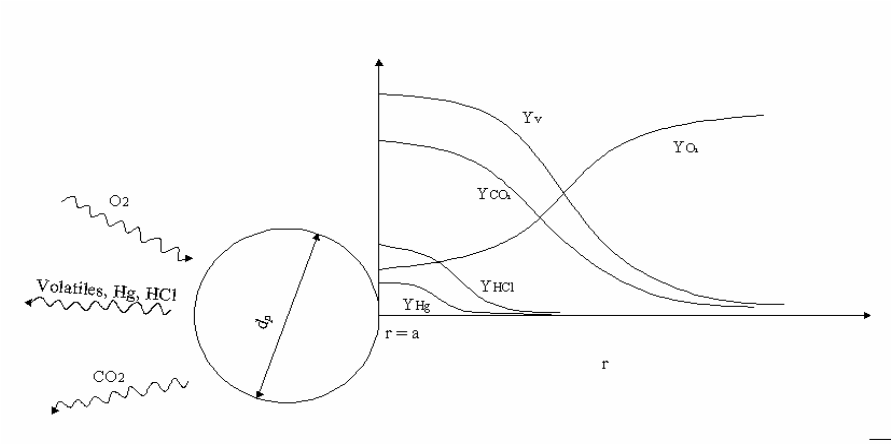

Fig A1. Illustration of burning of Coal particle

The following assumptions have been used for the transient ignition model:

1. Spherical symmetry exists and ρD = constant.
2. The coal particles are dry and ash free.
3. There is no relative motion between the particle and the gas.
4. The coal particle temperature is time dependent but spatially uniform.
5. The isothermal particle evolves volatiles uniformly throughout the particle. Devolatilization is endothermic and follows two competing routes with first order kinetics.
6. The rate of oxidation of volatiles is described by a global kinetic expression.
7. The ideal gas law is applicable.
8. Mercury and chlorine are released from a coal particle at a rate similar to its devolatilisation rate.
9. Elemental mercury and HCl are considered to be the volatile products of mercury and chlorine respectively. They exist in trace amounts.

PYRLOYSIS MODEL FOR MERCURY AND CHLORINE

The rate at which mercury and chlorine are released is assumed to be similar to the volatile release rate.[Shao], found that 90% of chlorine is released as HCl during pyrolysis of coal.

The volatile products of mercury and chlorine are assumed to be elemental mercury and HCl.

$$\dot{m}_{Hg} = f_{Hg,v}\,\dot{m}_v \qquad (1)$$

$$\dot{m}_{HCl} = f_{Cl,v}\,\dot{m}_v \qquad (2)$$

CONSERVATION EQUATIONS

Considering spherical symmetry, the conservation equations for mass, species and energy are given below.

Mass:
Assuming spherical symmetry, the mass conservation is written as

$$4\pi r^2\left(\frac{\partial \rho}{\partial t}\right)+\left(\frac{\partial \dot{m}}{\partial r}\right)=0 \qquad (3)$$

The mass flow rate ($\dot{m}$) includes the mass displaced/added through temperature gradient in the gas phase, the liberation rate of volatiles ($\dot{m}_v$), and the carbon mass loss rate ($\dot{m}_c$).

Species:
Assuming spherical symmetry, the species conservation is written as

$$4\pi r^2\rho\left(\frac{\partial Y_k}{\partial t}\right)+\dot{m}\left(\frac{\partial Y_k}{\partial r}\right)-\left[\frac{\partial}{\partial r}\left(4\pi r^2\rho D\left(\frac{\partial Y_k}{\partial r}\right)\right)\right]=w_{ch,k}^{'''}4\pi r^2 \qquad (4)$$

The species k are produced or consumed in the gas phase from pyrolysis reactions and homogeneous gas-phase reactions.

Energy:
Assuming spherical symmetry, the energy conservation is given as

$$4\pi r^2\rho\left(\frac{\partial h_T}{\partial t}\right)+\dot{m}\left(\frac{\partial h_T}{\partial r}\right)-\left[\frac{\partial}{\partial r}\left(4\pi r^2\rho D\left(\frac{\partial h_T}{\partial r}\right)\right)\right]=w_h^{'''}4\pi r^2 \qquad (5)$$

BOUNDARY CONDITIONS

The boundary conditions at r = *a* for Hg are as follows:

Mass:

$$\dot{m}_w=\dot{m}_v+\dot{m}_c+\dot{m}_{Hg}+\dot{m}_{Cl} \qquad (6)$$

The mass flow rate at the interface must equal the mass loss rate by the particle via volatiles ($\dot{m}_v$), carbon oxidation ($\dot{m}_c$), mercury ($\dot{m}_{Hg}$) and chlorine ($\dot{m}_{Cl}$). The liberation rate of volatiles is modeled using a competing reaction model [Annamalai, 2006]; See [Du and Annamalai] for other boundary conditions

Species
The changes made to the boundary conditions in order to incorporate the mercury and chlorine chemistry are:

$$\dot{m}_w Y_{Hg,w} - \rho D \left(\frac{\partial Y_{Hg}}{\partial r} \right)_{r=a} 4\pi a^2 = \dot{m}_{Hg} \tag{7}$$

$$\dot{m}_w Y_{HCl,w} - \rho D \left(\frac{\partial Y_{HCl}}{\partial r} \right)_{r=a} 4\pi a^2 = \dot{m}_{HCl} \tag{8}$$

NUMERICAL PROCEDURE

An explicit upwind scheme is used to solve the equations. The domain outside of the particle surface is divided into 10 spherical shells in the radial direction. The source terms w_h''' and $w_{ch,k}'''$ with Tp = $(Tp)_0$ was calculated with the given conditions at t = 0 for $(T)_o$, $(Y_k)_o$, $(m_p)_o$, $(Tp)_o$, $(Pp)_o$, and $(dp)_o$. The properties at t = Δt, 2Δt, 3Δt,. .. etc., were determined repeatedly by using the source terms and the explicit method.

MERCURY REACTION MECHANISM

A three step reaction is implemented for the oxidation of mercury. Wet carbon monoxide reaction scheme is considered. Equilibrium reaction chemistry is considered for H_2O. The radicals which are more reactive will help in the formation of atomic chlorine. The OH radical formed during equilibrium results in atomic chlorine when reacted with HCl. This atomic chlorine sets the rate oxidation of mercury. The kinetics for the following three step reaction mechanism is taken from [Widmer et al] and [Rosler et al].

	A cm,mol,sec	Ea cal/mol
HCl + OH → Cl + H_2O	2.71E07	-220
Hg + Cl + M →HgCl + M	2.4E8	-14400
HgCl + Cl + M → $HgCl_2$ + M	2.19E18	3100

DATA INPUT

For the present numerical simulations, dry ash free Texas lignite coal is considered. Table A1 shows the composition of coal on DAF basis. It also shows the base conditions. The effect of the change in chlorine concentration, particle diameter and ambient temperature are considered in order to study their effect on mercury oxidization.

Table A1. Coal Properties and Base case conditions

Volatile Matter	49.38
Fixed C	50.62
Heat of Combustion	23MJ/kg
%C	74.06
%H	4.40
%N	1.35
%S	1.22
%O	19.14
Cl	200ppm
Hg	120ppb
Density	1300kg/m3
Ambient Temperature (T_∞)	1500K
Particle Diameter (d_p)	100microns

It is known from the literature studies that increase in chlorine concentration in flue gases will result in increase oxidation of mercury. In order to increase the chlorine concentration, coal is blended with feedlot biomass. Feedlot biomass has much higher concentration of chlorine as compared to Texas lignite coal. Coal is blended with feedlot biomass in the ratios of 90:10 and 80:20. Table A2 shows proximate and ultimate analysis of coal, feedlot biomass and the coal blends.

EFFECT OF FB %

It is noted that the two competing reactions are valid only for coal. The blended fuel is treated like a single particle. As the percentage of feedlot biomass is increased, there is an increase in the total volatile yield essentially due to higher proximate VM.

Table A3 shows the percentage of mercury oxidized to $HgCl_2$ with increase in % FB. The chlorine liberated as HCl with FB, promotes the oxidation of Hg. For the base case, where the chlorine concentration is 140 ppm, the percentage of mercury oxidized is around 11%. At 20% of FB almost 90% of Hg gets oxidized to $HgCl_2$.

Table A2. Proximate and ultimate analysis of the fuel

	Texas-Lignite	Feedlot Biomass	Texas Lignite-Biomass(90:10)	Texas Lignite-Biomass(80:20)
Proximate (%)				
Volatile	49.38	81.84	52.63	55.87
Fixed C	50.62	18.19	47.38	44.13
Ultimate (%)				
Carbon	74.06	52.55	71.91	69.76
Hydrogen	4.40	6.35	4.60	4.79
Nitrogen	1.35	4.71	1.69	2.03
Sulfur	1.22	1.03	1.20	1.18
Oxygen	19.14	35.36	20.76	22.39
Chlorine (ppm)	200	9096	1089	1979
Mercury (ppb)	120	6	108	97
HHV(kJ/kg)	23200	7861	21639	20108