RICE

COAL COMBUSTION: EFFECT OF PROCESS CONDITIONS ON CHAR REACTIVITY

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PROJECT OBJECTIVES

The project will quantify the effect of the following pyrolysis conditions on the macropore structure and on the subsequent reactivity of chars: (a) pyrolysis heating rate; (b) final heat treatment temperature (HTT); (c) duration of heat treatment at HTT (or soak time); (d) pyrolysis atmosphere (N_2 or O_2/N_2 mixtures); (e) coal particle size (100 - 1,000 μm in diameter); (f) sulfur-capturing additives (limestone); and (g) coal rank. Pyrolysis experiments will be carried out for three coals from the Argonne collection: (1) a high-volatile bituminous coal with high ash content (Illinois #6), (2) a bituminous coal with low ash content (Utah Blind Canyon) and (3) a lower rank subbituminous coal (Wyodak-Anderson seam).

Task A: We will obtain the time histories and follow the fate of single particles during pyrolysis in our TGA/VMI reactor. The experiments will be videotaped and digital images at several time instants will be acquired and analyzed on the image processor. For each run, we will measure particle swelling and shape, as well as the number and size of volatile bubbles evolving from each particle. For selected sets of conditions, several char samples will be collected and polished sections will be prepared so that we can accurately analyze the internal structure of the char particles. We will pay particular attention to the existence of correlations between particle swelling and macropore surface area as well as to the fate of ash inclusions during pyrolysis.

Task B: A different set of pyrolysis experiments will be immediately followed by combustion experiments. Without removing the particles from the TGA/VMI reactor, the char samples will be reacted with O_2 to complete conversion at high temperatures. Different gas flow rates of gases and O_2 concentrations will be used to investigate the effect of external mass transfer limitations. Issues to be addressed in this study will include the influence of particle swelling and ash content on thermal ignitions.

Task C: We will use mathematical models to simulate combustion of char particles in the regime of strong diffusional limitations. Digitized particle cross-sections obtained from our studies will be used as computational grids for these simulations and the average behavior will be obtained by analyzing a large number of particle cross-sections. The observed reactivity vs. conversion patterns will be analyzed and classified. These patterns will then be used in transient models to describe ignition and extinction phenomena in char combustion.

1. SUMMARY

A systematic parametric study was carried out in the past quarter to quantify the effect of different process parameters on the ignition phenomena. Using the mathematical model presented in the previous quarterly report, we investigated how char properties (porosity, particle size, macropore surface area, and micropore radius) and operating conditions (oxygen concentration, flow rate) affect ignition phenomena. In every case, we clearly identified the temperature range in which thermal ignitions may be expected. Model predictions will next be compared to experimental results to validate our theoretical model.

2. EFFECTS OF REACTION CONDITIONS AND CHAR PROPERTIES ON CHAR IGNITION

Table 1 lists the base values of the model parameters used for our parametric study. These values correspond to chars with open macropore structure produced by devolatilizing Illinois #6 coal at high heating rates.

Table 1
Base values of Char Properties and Operating Conditions

Parameters	Base Value
Oxygen Concentration	33%
Particle Diameter	0.39 mm
Macroporosity	0.72
Macropore Surface Area	$2951 \text{ cm}^2/\text{cm}^3$
Micropore Radius	5 Å
Bulk Velocity	0 cm/s (stagnant fluid)

2.1 Oxygen concentration

Figure 1 shows how the solid temperatures T_s expected for our char vary with

the ambient temperature T_f for several oxygen concentrations. As the oxygen concentration increases beyond a certain level, the T_s vs. T_f curves take the classical hysteresis form indicating the existence of multiple solutions. As is well known, the upper and lower solutions correspond to an ignited and unignited steady-state respectively.

To facilitate comparison of model predictions with experimental data, we will use two temperatures to characterize the multiplicity range in each case: (1) the minimum temperature T_L at which multiplicity can occur and (2) the upper temperature limit T_U of the multiplicity region. When the ambient temperature is smaller than T_L , we have only one steady-state solution corresponding to a low particle temperature. For ambient temperatures in the range $T_L < T_f < T_U$, we have three steady-state solutions for the particle temperature, while for ambient temperatures above T_U , the particle can exist only in the ignited state characterized by a high solid temperature T_s .

Figure 1 shows that the oxygen concentration has a significant influence on the onset of particle ignitions. High oxygen concentrations reduce the minimum ignition temperature T_L and broaden the multiplicity region. For a particular ambient temperature in the multiplicity region, the ignited particle temperature increases with increasing oxygen concentration.

The effect of oxygen concentration on the multiplicity region is shown more clearly on Figure 2 where the temperature limits of the multiplicity region are plotted as a function of bulk oxygen concentration. As the oxygen concentration decreases, the multiplicity region shrinks. The minimum ignition temperature increases rapidly as the oxygen concentration decreases, while the upper limit shows a very small decrease.

2.2 Particle size

The effect of particle size on the multiplicity region is shown in Figure 3. As expected, these results indicate that larger particles ignite more easily since they are less effective than smaller particles in removing the heat generated by the reaction. No multiple steady states are predicted for particles smaller than 0.1 mm in diameter. As the size decreases, the multiplicity region shrinks as depicted in the plots of T_L and T_U vs. particle diameter of Figure 4.

Our model predictions agree with the predictions of the distributed model developed by Sotirchos and Amundson [1, 2]. Their studies concluded that the minimum ignition temperature decreases with increasing particle size. The larger particles have a lower external surface to volume ratio and the heat removal is less efficient. Therefore, particle overheating and thermal ignition take place at lower ambient temperatures.

2.3 Macroporosity and Macropore Surface Area

Figure 5 shows the effect of char particle macroporosity on the multiplicity region. Particles with more open macropore structure will ignite more easily, since their pore surface area is more accessible to the gaseous reactants. The resulting decrease in intraparticle diffusional limitations leads to higher rates of reaction and heat generation. Figure 6 shows that the upper temperature limit of the multiplicity region T_U is virtually independent of macroporosity, while the minimum ignition temperature T_L decreases with increasing macroporosity. At very low macroporosity (less than 0.35), only one steady solution is possible.

The macropore surface area has a similar effect on the multiplicity region, since the reaction rate in the regime of diffusional limitations becomes proportional to the surface area of the macropores. Figures 7 and 8 show the effect of macropore surface area on the multiplicity region. Particles with high macropore surface areas will ignite more easily than particles with low macropore surface areas. Again, the upper temperature limit T_U of the multiplicity region is virtually independent of the surface area of macropores S_g while the minimum ignition temperature T_L decreases with increasing S_g . The behavior shown in Figures 7 and 8 is expected since larger macropore surface areas enhance the reaction rate and increase the rate of heat generation inside the particle.

2.4 Micropore Radius

The model also predicts that increases in the average micropore radius will decrease the minimum ignition temperature and widen the multiplicity region. This effect is shown in Figures 9 and 10. When the average micropore radius increases, diffusional limitations in the micropores will diminish making more

surface area available for reaction and increasing the combustion rates. Figure 10 shows that the minimum ignition temperature T_L decreases very rapidly as the micropore radius increases from 1 Å to 6 Å. For micropore radii larger than 6 Å, the minimum ignition temperature is almost independent of the micropore radius. Except for a very small drop for small micropore radii, the upper temperature limit of the multiplicity region T_U remains constant at about 740 °C.

2.5 Fluid Velocity

The velocity of the ambient gas flowing around a burning particle has a strong influence on the rates of external mass and heat transfer. Until now, only stagnant fluid around the particle was considered. The assumption of stagnant flow is valid for the particles located in the middle of the TGA sample pan. However, particles close to the edges of the pan should experience significant fluid velocities.

Our model was also used to study the effect of fluid velocity. Figures 11 and 12 present the model predictions for various fluid velocities around the particle. These plots reveal that the minimum ignition temperature increases with increasing flow rate. High gas flow rates increase the heat transfer coefficient, thus enhancing the heat removal rates and preventing thermal ignition at low ambient temperature. These predictions agree with our earlier experimental results [3].

2.6 Conclusions from Parametric Study

Our model predicts that the likelihood of particle ignition increases with

- increasing oxygen concentration,
- increasing particle size,
- increasing macroporosity,
- increasing macropore surface area,
- increasing micropore radius, and
- decreasing fluid velocity of the ambient gas.

3. REFERENCES

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Figure 1: Model predictions of the effect of oxygen concentration on char ignition.

Figure 2: Effect of oxygen concentration on the multiplicity region.

Figure 3: Model predictions of the effect of particle size on char ignition.

Figure 4: Effect of particle size on the multiplicity region.

Figure 5: Model predictions of the effect of macroporosity on char ignition.

Figure 6: Effect of macroporosity on the multiplicity region.

Figure 7: Model predictions of the effect of macropore surface area on char ignition.

Figure 8: Effect of macropore surface area on the multiplicity region.

Figure 9: Model predictions of the effect of micropore radius on char ignition.

Figure 10: Effect of micropore radius on the multiplicity region.

Figure 11: Model predictions of the effect of fluid velocity on char ignition.

Figure 12: Effect of fluid velocity on the multiplicity region.