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COAL COMBUSTION: EFFECT OF PROCESS CONDITIONS ON CHAR REACTIVITY

Quarterly Technical Report

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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 mm 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

During the past quarter, we systematically investigated the effects of particle size, pyrolysis heating rate, and heat treatment temperature on the reactivity of chars. The results show that pyrolysis heating rates or particle size do not affect the reactivity of chars in the kinetic control regime (420 °C). High heat treatment temperatures (HTT) slightly lowered the char intrinsic reactivities.

When the char particles were reacted in the regime of diffusional limitations (625 °C), a significant effect of particle size was detected. We observed that decreasing final heat treatment temperatures resulted in small increases of the intrinsic reactivity for the smallest particles. For the largest particles, however, the effect of decreasing HTT was dramatic. By lowering the HTT from 775 to 625 °C, the reactivity of chars at 625 °C increased by a factor of 6 for chars produced from 20-25 mesh coal particles. Finally, the shape of the reactivity patterns changed significantly as we moved from the regime of kinetic control to the regime of intraparticle diffusional limitations

2. EFFECT OF PROCESS CONDITIONS ON REACTIVITY (TASKS A AND B)

Experimental Procedures

Using the thermogravimetric reactor with video microscopy imaging (TGA/VMI), we studied three size fractions of Illinois #6 coal : 20-25 mesh (710-840 μm), 28-32 mesh (500-600 μm) and 50-60 mesh(250-300 μm). To prevent agglomeration of the pyrolyzing particles, 2, 8, and 25-35 particles were placed on the sample pan for each run with the 20-25, 28-32 and 50-60 mesh size fractions respectively.

The experimental conditions for the sequential pyrolysis and combustion runs are listed in Table 1.

TABLE 1
Experimental Conditions for Pyrolysis and Combustion

Pyrolysis Stage: Rate : 1 and 20 °C/s Heat Treatment Temperature (HTT): 550, 625, and 700 °C Soak Time: 3 min. Flowing gas: 100% nitrogen
Combustion Stage: Reaction Temperature: 420 and 550 C Flowing gas: 21% Oxygen Gas flow rate: 360 sccm..

The results from these experiments indicate that with 21% oxygen in the ambient gas, a reaction temperature of 550 °C is not high enough for the particles to react in the regime of strong diffusional limitations. For this reason, we performed another set of experiments at a higher reaction temperature (625 °C). Since we always keep the combustion temperature below the HTT, three heat treatment temperatures of 625, 700, and 775 °C were used for these experiments.

Results and Discussion

Since the reactivity of chars changes continuously with conversion, comparisons among chars should be based on the entire reactivity pattern and not on single point reactivities (i.e. maximum rate). Even average reactivities (i.e. average reaction rate for a given range of conversions) may not give a satisfactory picture of the reactivity patterns.

For our comparisons, we will plot the reactivity patterns $R_S(x)$ vs. conversion x where the reaction rate R_S is defined by

$$R_s = \frac{1}{m(t)}\left(\frac{dm}{dt}\right) \tag{1}$$

For this definition, $m(t)$ is the mass of char remaining unreacted at time t and $\left(dm/_{dt}\right)$ is the instantaneous rate of reaction. The conversion x is defined as

$$x = \frac{m_0 - m(t)}{m_0} \tag{2}$$

where m_0 is the initial mass of unreacted char and $m(t)$ is the mass of char that remains at time t after the start of the experiment.

Figure 1 presents the reactivity patterns of several chars combusted with 21% oxygen at 420 °C. These chars were produced from three different coal particle sizes and different pyrolysis heating rates (1 and 20 °C/s), but with the same heat treatment temperature. At these reaction conditions, all char particles react in the regime of kinetic control.

The graphs of Figure 1 show that particle size and pyrolysis heating rates do not affect the reactivity pattern when the chars react in the kinetic control regime. Intrinsic reactivities increase with conversion due to the increasing accessibility and specific surface area of the enlarging micropores. In the kinetic control regime, the micropores are fully utilized and reaction rates are proportional to the total active area. Thus, the results of Figure 1 indicate that the chars of Figure 1 have similar intrinsic surface reactivities and micropore structures.

To determine whether the heat treatment temperature (HTT) affects reactivities in the kinetic control regime, Figure 2 presents the reactivity patterns for several chars produced from 20-25 mesh coal particles at different pyrolysis heating rates and HTT. The chars produced at 1 °C/s show a slight decrease in reactivity with increasing heat treatment temperature, in agreement with previous data from the literature and our laboratory. We must note though that these changes in intrinsic reactivity are small and appear to be within the reproducibility error of our experiments. The char produced at 20 °C/s with 700 °C HTT exhibits higher reactivity than the corresponding 1 °C/s char. The overall conclusion from Figure 2, however, is that all reactivity patterns are similar indicating that the chars have similar intrinsic surface reactivities and micropore structure.

A different way to present the reactivity patterns is to plot the reaction rate R_0 vs. the conversion x. The reaction rate R_0 is defined as follows

$$R_0 = \frac{1}{m_0}\left(\frac{dm}{dt}\right) \tag{3}$$

where m_0 is the initial mass of unreacted char and $\left(dm/_{dt}\right)$ is the instantaneous rate of reaction. The reaction rates R_0 can be computed from R_s using the formula

$$R_0 = R_s(1-x) \tag{4}$$

x is the conversion.

Figure 3 shows some of the reactivity patterns R_0 vs. x for combustion at 420 °C. These patterns show the characteristic smooth maximum in R_0 at about 30-40 % conversion as predicted by the random pore models for reaction with full utilization of the micropores. This pattern is another indication that reaction occurs in the regime of kinetic control. We should note here that the reactivity of a char produced at a pyrolysis rate of 20 °C/s seems to be slightly higher than the rate of the same char pyrolyzed at 1 °C/s.

The reaction temperature of 550 °C is probably in the intermediate temperature range separating the kinetic control and diffusion limited regimes. This fact can be seen by comparing Figures 3 and 4 that show the reactivity patterns of various chars combusted at 550 °C to previous and subsequent Figures.

Figure 4 shows small reactivity differences among chars produced from coal particles of different sizes at 1 °C/s. The two chars produced at 20 °C/s show a different reactivity pattern with a sharp increase at low conversions and a leveling off at intermediate conversions. This is reminiscent of ignition patterns we have observed before. Thermal particle ignitions usually occur as the particles reach their final reaction temperature.

Figure 5 shows the effect of heat treatment temperatures on the reactivity of chars produced from coal particles from the 28-32 mesh range. Low heat treatment temperatures (550 °C) produce chars that are significantly more reactive at this temperature. Reactivity differences diminish with higher heat treatment temperatures (e.g. compare the curves for 625 °C and 700 °C HTT).

Figures 6 through 8 present reactivities at 625 °C for chars produced under various pyrolysis conditions. At this reaction temperature, the reaction is in the diffusion limited regime. In this regime, the reaction rates R_s generally increase rapidly in the early stages of combustion, reach a maximum and then level off to an almost constant-rate plateau.

Figure 6 shows the reactivity patterns R_s vs. x for chars produced from the smallest coal particles (50-60 mesh). The heat treatment temperature (HTT) clearly affects the reactivity of the chars as the reactivity increases by almost a factor of 2 when the HTT decreases from 775 to 625 °C.

Figure 7 shows that chars produced from the 28-32 mesh coal particles show larger increases in reactivity with decreasing HTT. The char produced at 625 °C HTT in particular shows a very sharp initial increase in reactivity.

Finally, Figure 8 presents the reactivity results for the largest char particles (coal particle size 20-25 mesh). The reactivity of the 20-25 mesh sample produced at 775 °C HTT is similar to the reactivities of the 50-60 mesh and 28-32 mesh samples produced at the same HTT. However, the 20-25 mesh sample produced at 625 °C HTT shows much larger reactivity than of the samples produced from smaller particles. The effect of particle size increases sharply with decreasing HTT.

The observed effect of the particle size is consistent with our theoretical analysis of thermal particle ignitions. Increasing particle sizes decrease the rate at which heat is removed from a reacting particle. If the heat production rate due to chemical reaction remains the same, the particle temperature will rise increasing the observed reaction rate.

Although the reactivity patterns indicate thermal particle ignitions, such ignitions were not visible in the video sequences in the form of luminous flames. Only sudden and rapid consumption of the particles was observed on the video sequences. This shows that the particles reacted at temperatures higher than the ambient temperature of 625 °C, but lower than the temperatures required to produce a luminous flame.

The particle temperature and the luminosity of the ignition flame increases with oxygen composition in the flowing gas. At low oxygen concentration, the reaction does not produce sufficient heat to cause particle overheating. Previous experimental results have shown that ignitions are visible when 33% oxygen concentration is used in the combustion stage.

Future Work

In the next quarter, the investigation of the effect of process conditions on char reactivity will continue. We will repeat many of the experiments discussed here to asses the reproducibility error for the experiments. Also, we will investigate the effect of oxygen concentration by performing combustion experiments with different oxygen concentration. Our previous experimental results have shown that ignitions are visible on the video sequences when 33% oxygen concentration is used.

We will also continue our work on developing a simple model that can predict the effects of pyrolysis and combustion process conditions on the thermal ignitions of char particles.

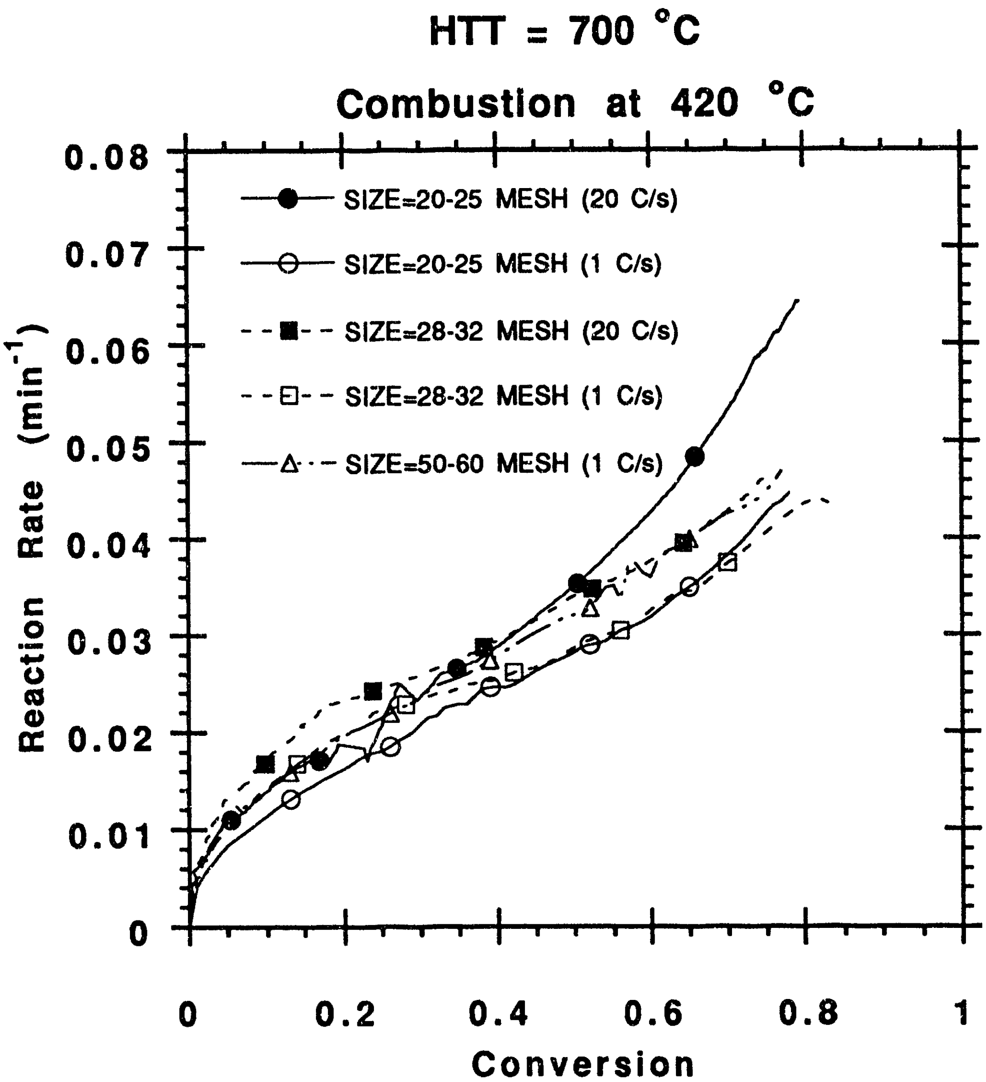

Figure 1: Intrinsic reaction rates for chars produced at various pyrolysis heating rates from coal particles of three different sizes. Heat treatment temperature for all runs is 700 °C.

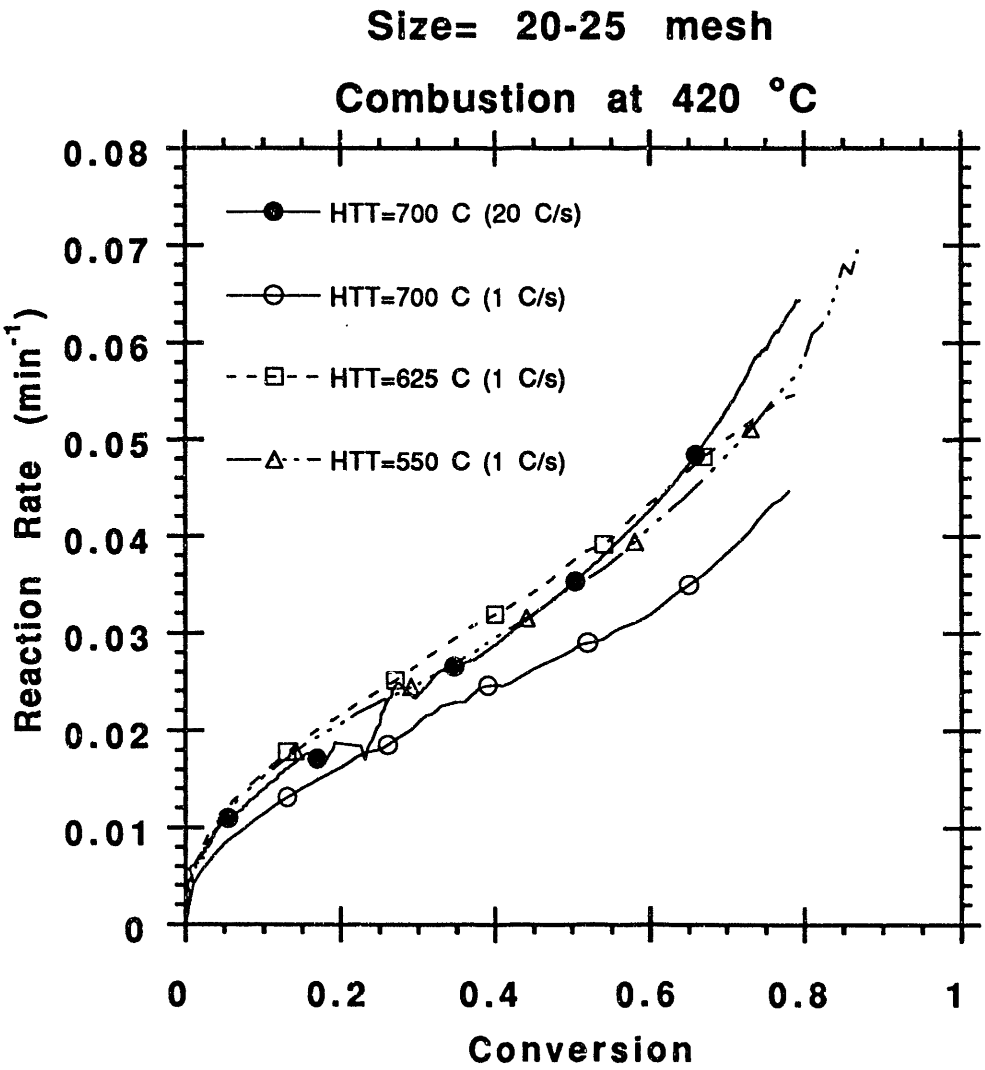

Figure 2: Intrinsic reaction rates for chars produced at various pyrolysis heating rates and heat treatment temperatures from coal particles in the 20-25 mesh size range.

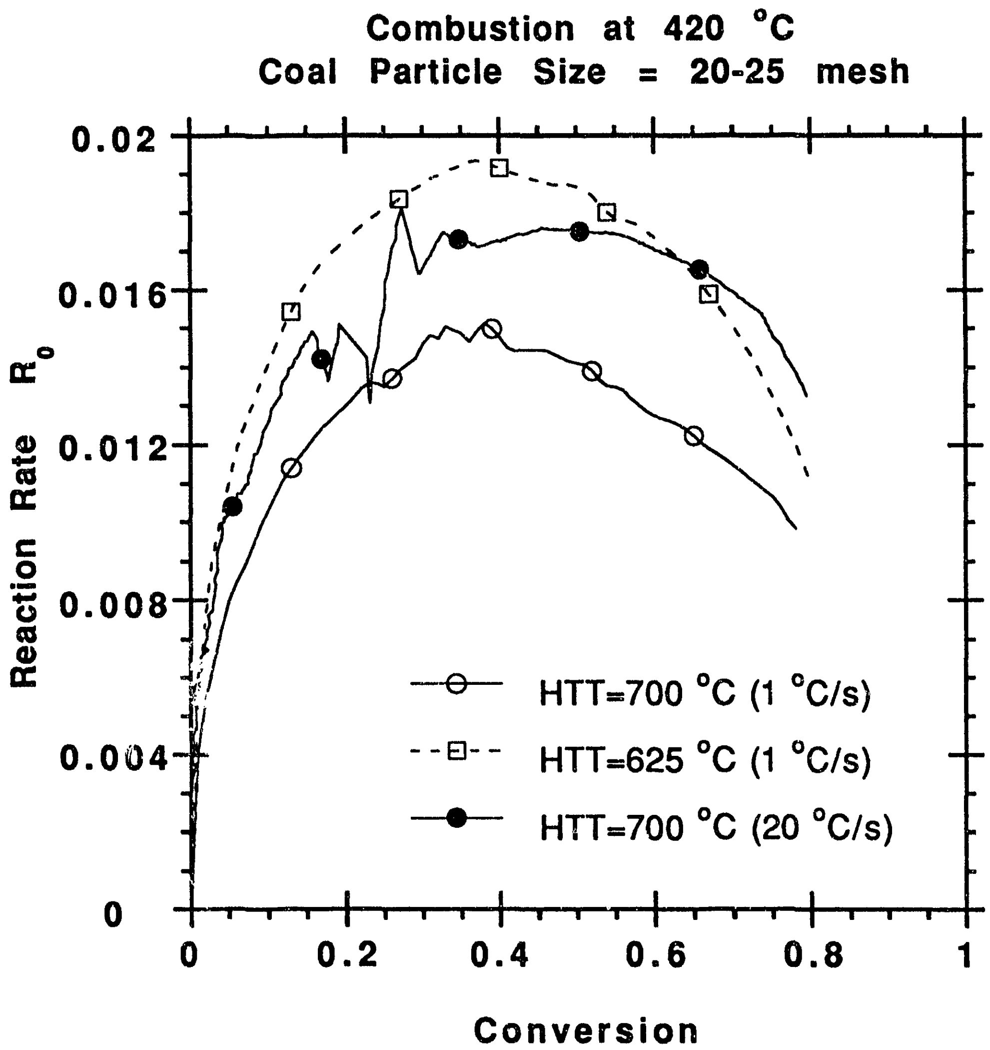

Figure 3: Reaction rate R_0 vs. conversion patterns for chars produced at various pyrolysis heating rates and heat treatment temperatures from coal particles in the 20-25 mesh size range.

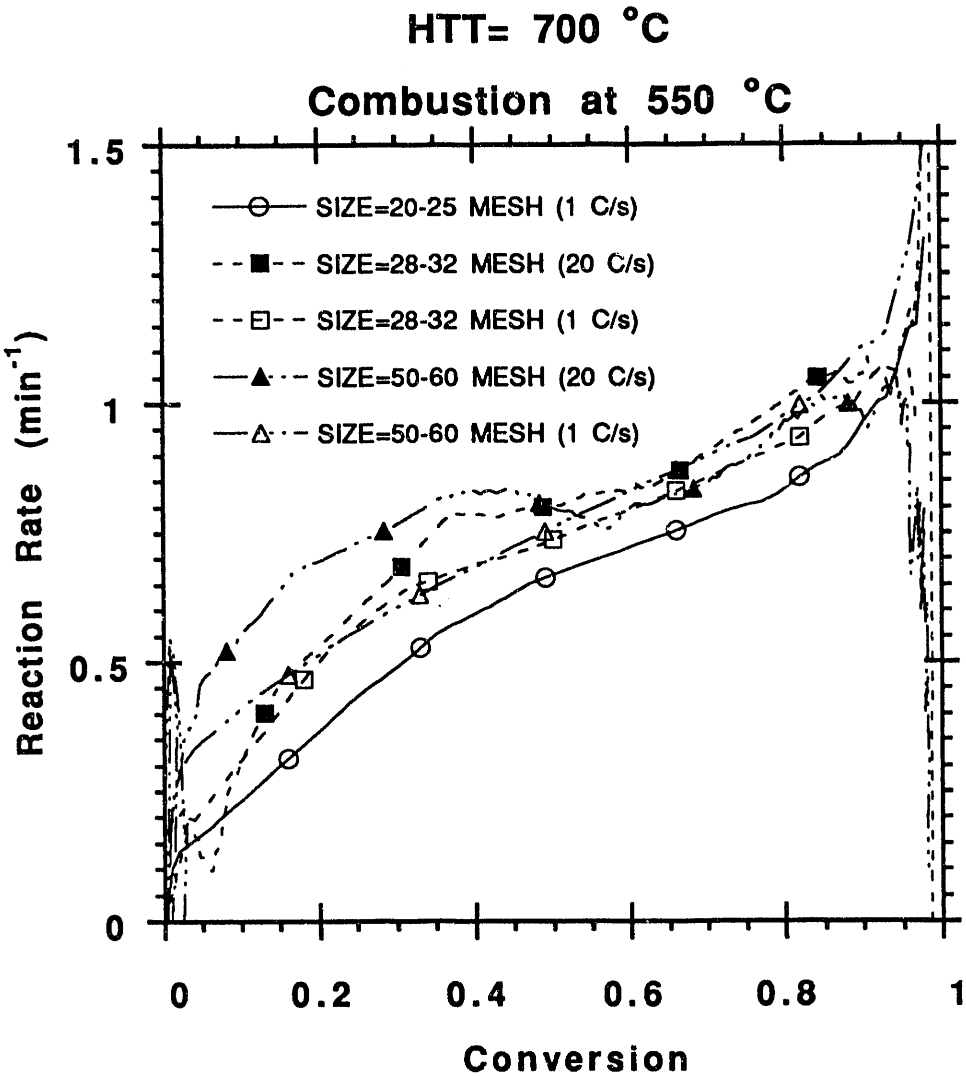

Figure 4: Reaction rate R_s vs. conversion patterns for combustion at 500 °C of chars produced at various pyrolysis heating rates from coal particles of three different sizes. Heat treatment temperature for all chars was 700 °C.

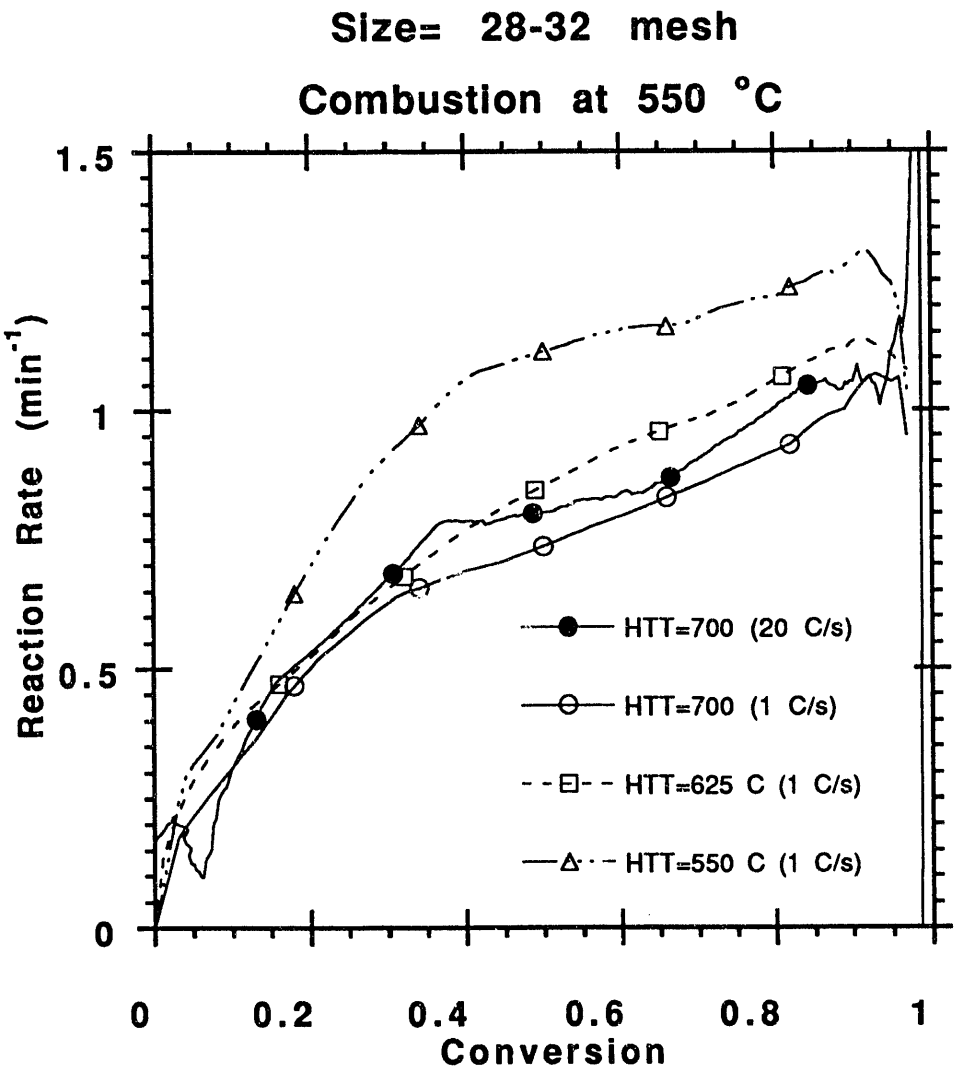

Figure 5: Reaction rate R_s vs. conversion patterns for combustion at 550 °C of chars produced at various pyrolysis heating rates and heat treatment temperatures. Coal particle size was in the 28-32 mesh range for all samples.

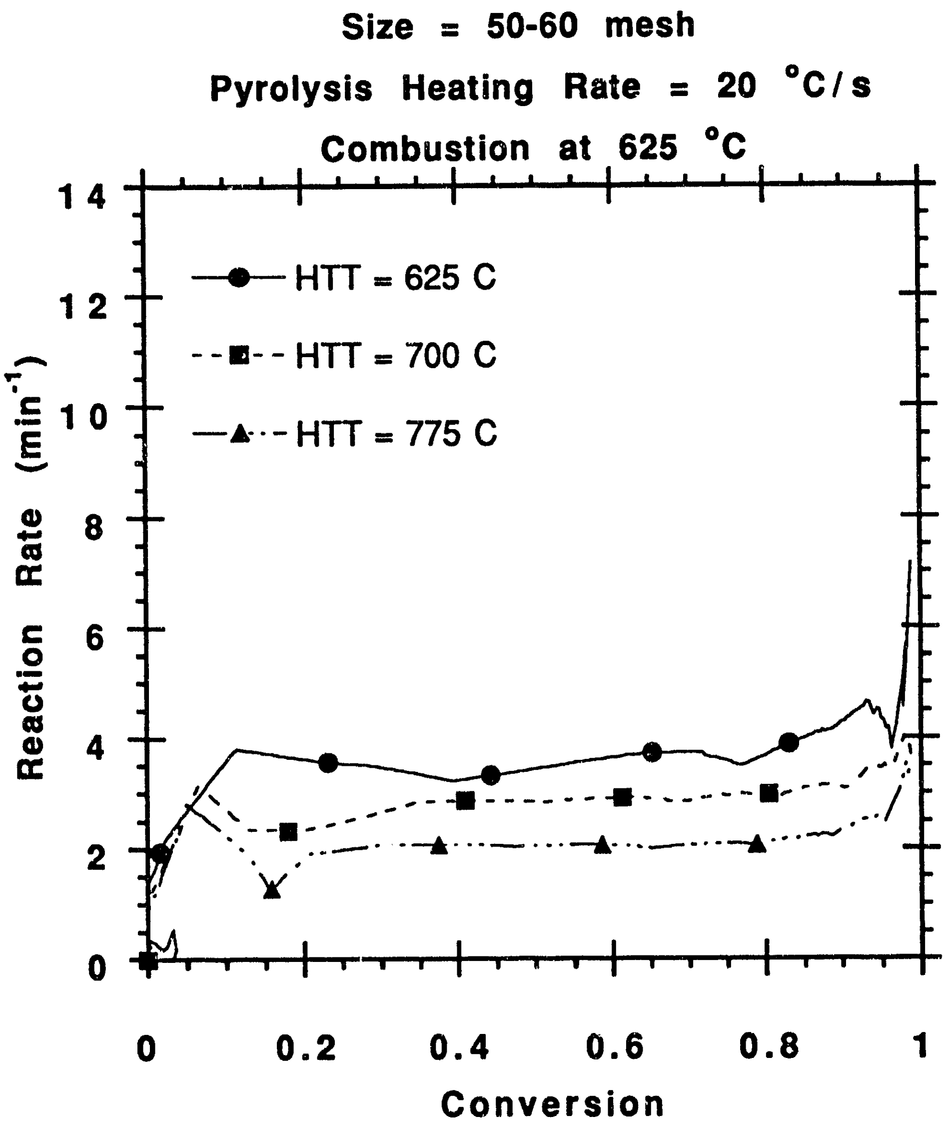

Figure 6: Reaction rate R_s vs. conversion patterns for combustion at 625 °C of chars produced at various heat treatment temperatures and a pyrolysis heating rate of 20 °C/s. Coal particle size was in the 50-60 mesh range for all samples.

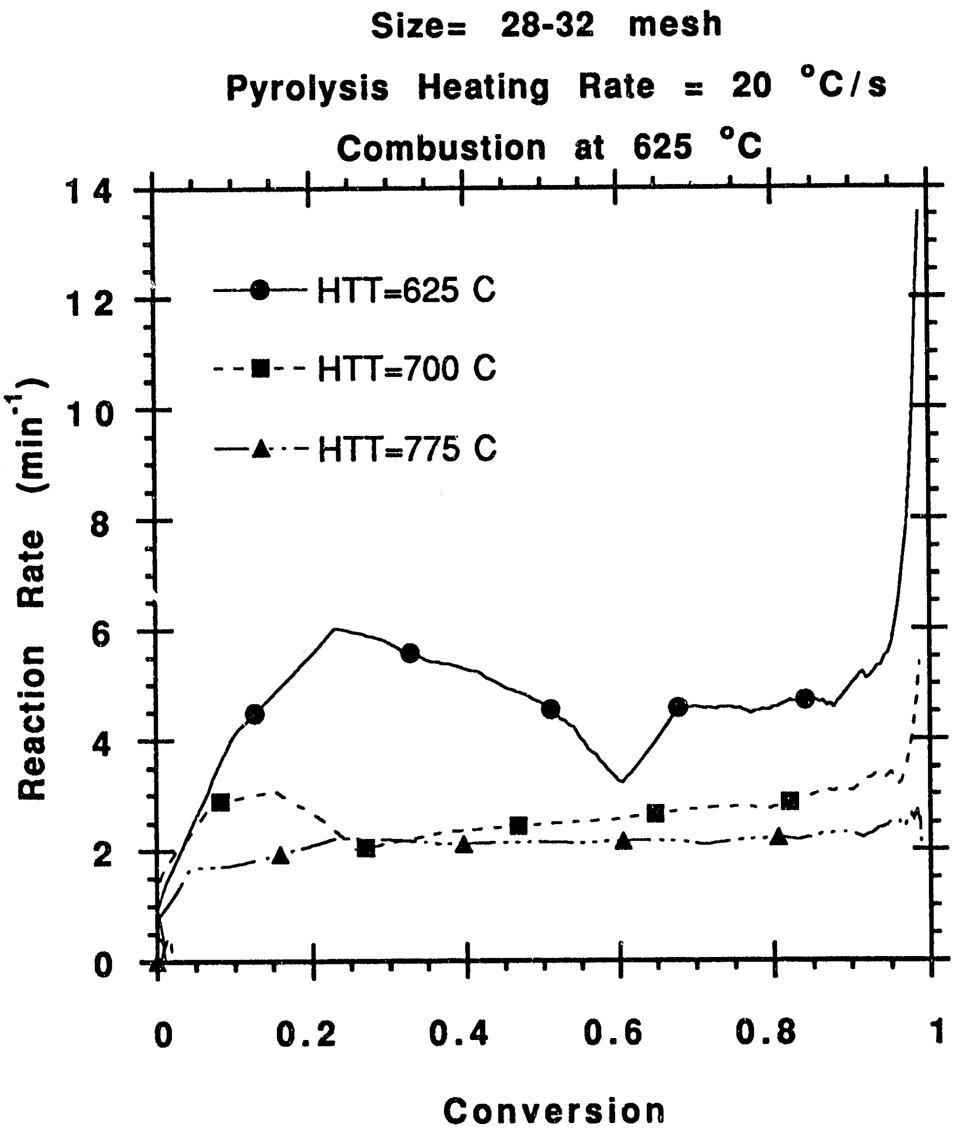

Figure 7: Reaction rate R_s vs. conversion patterns for combustion at 625 °C of chars produced at various heat treatment temperatures and a pyrolysis heating rate of 20 °C/s. Coal particle size was in the 28-32 mesh range for all samples.

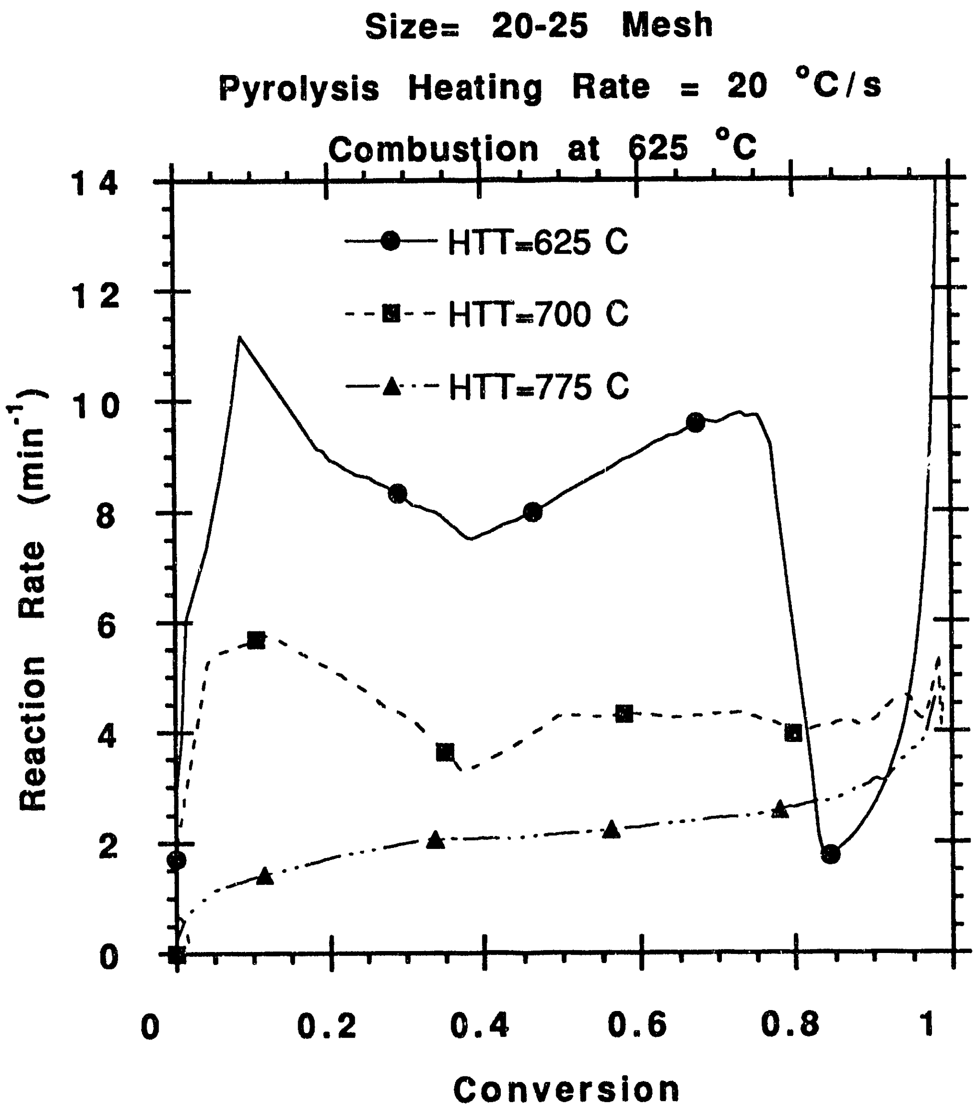

Figure 8: Reaction rate R_s vs. conversion patterns for combustion at 625 °C of chars produced at various heat treatment temperatures and a pyrolysis heating rate of 20 °C/s. Coal particle size was in the 20-25 mesh range for all samples.

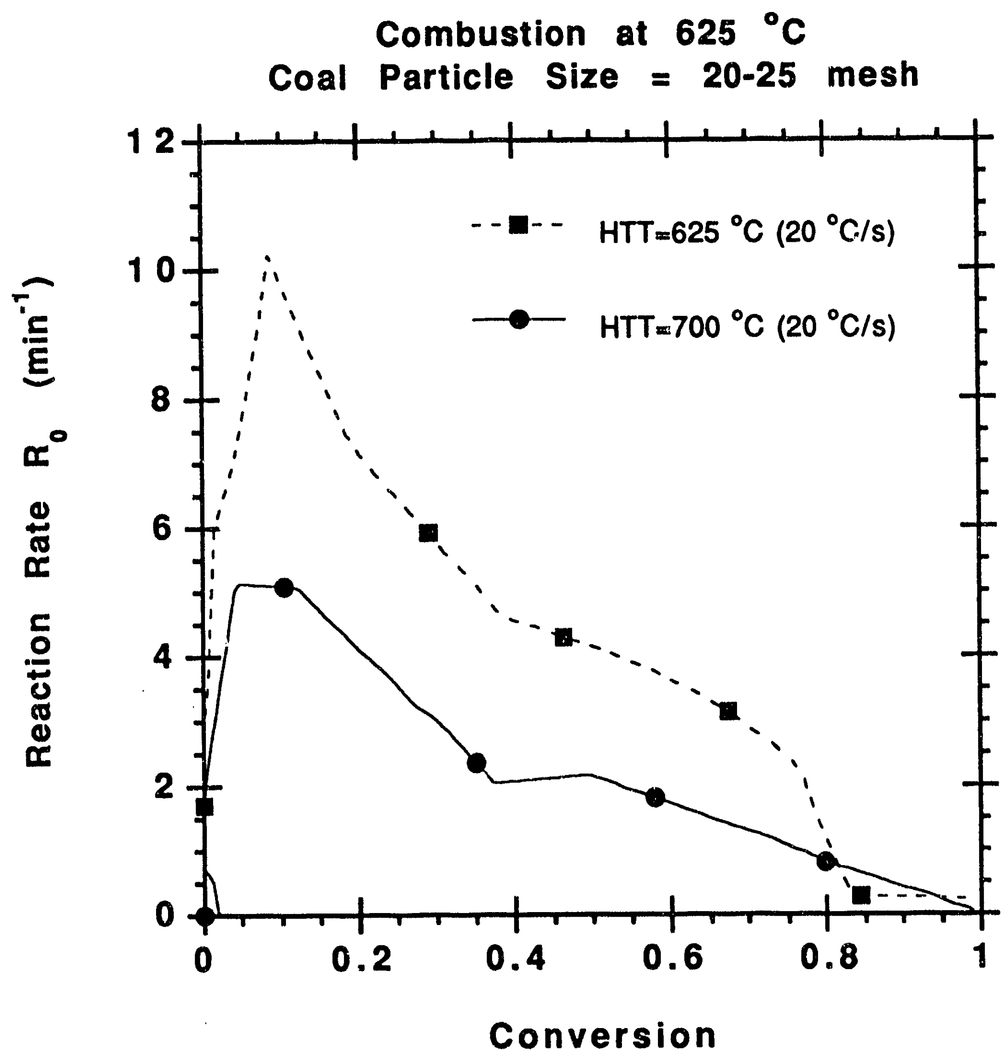

Figure 9: Reaction rate R_0 vs. conversion patterns for combustion at 625 °C of chars produced at two heat treatment temperatures and a pyrolysis heating rate of 20 °C/s. Coal particle size was in the 20-25 mesh range for both samples.

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