REACTIVITIES OF CHARS OBTAINED AS RESIDUES IN SELECTED COAL CONVERSION PROCESSES

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ABSTRACT

    Reactivities in 0.1 MPa of air of seven chars obtained as residues in selected coal conversion processes have been determined at temperatures below their processing conditions. Even though reactivities vary by some 200 times, activation energies for reaction, as determined from Arrhenius plots, are all close to 130 kJ/mole. Differences in reactivities are related to differences in parent coal rank and residence times and temperatures used upon the conversion of the coals to chars.

INTRODUCTION

    The overall economics of many commercial and developing coal gasification and liquefaction processes are highly dependent on the reactivity of the residual char. For example, if the char is sufficiently reactive, it can be used to produce the (very expensive) H_2 necessary in liquefaction, via the char/steam reaction. On the other hand, if it is relatively unreactive, it can only be combusted for steam and/or power generation. In the production of liquids by coal pyrolysis, char is, indeed, the principal product [1]. Also, in short-residence-time gasification processes, such as, for example, the Rockwell hydrogasification process [2], or a hypothetical process simulated in an entrained-flow reactor, discussed in other parts of this study [3—6], a considerable amount of char is produced.
    It was shown recently [6] that the gasification reactivity of a lignite char produced in this laboratory is highly dependent on the temperature—time history of the coal during pyrolysis. This reactivity was placed into perspective by comparing it with that of chars and carbons of increasing purity and crystallinity [5]. The observed gasification behavior was rationalized in terms of the variation of active surface area caused by changes in pyrolysis conditions [3, 4]. It is of interest to investigate whether this fundamental approach can be used to understand, and hopefully predict, the gasification behavior of

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chars obtained in some of the above mentioned processes which are of immediate commercial interest.

EXPERIMENTAL

Char samples from selected coal conversion processes were obtained through cooperation with the Department of Chemical Engineering of Brigham Young University. They are listed in Table 1, together with the available information on their production conditions [7]. Procedures used for measuring reactivities in a TGA apparatus have been described previously [3—6, 8].

RESULTS AND DISCUSSION

Char reactivities in 0.1 MPa air are presented on an Arrhenius plot in Fig. 1 and on a normalized TGA plot in Fig. 2. Reaction conditions (temperature and time to reach 50% conversion) are given in Fig. 2. It is seen in Fig. 1 that the reactivities differ by as much as 200 times, the Occidental char being the most reactive and the Rockwell hydroliquefaction char (residence time 600 ms) being the least reactive. However, the activation energy is the same in all cases, about 130 kJ/mol, essentially identical to the value found for the lignite chars in other parts of this study [3—6].

Interpretation and meaningful comparison of the reactivities shown in Fig. 1 would require a better knowledge of the exact temperature—time histories of the chars and a thorough study of their physical properties, not available at the present time. Fundamental rate constants can be obtained on the basis of the active surface area of the chars, as has been shown recently by the authors [3, 4]. However, the existing general knowledge about these chars does allow a qualitative discussion which is in agreement and consistent with the results obtained in other parts of this study [3—6] for lignite chars produced in the laboratory under controlled pyrolysis conditions.

It is seen, for example, that the increase in hydroliquefaction residence time from 60 to 600 ms decreases the subsequent reactivity of the Rockwell bituminous char by a factor of about two. From the general knowledge of the composition and dispersion of the inorganic constituents in bituminous coals, catalysis is not expected to play a major role in the reactivity of the char. In lignite chars, where the catalytic effect of CaO was shown to be dominant [4], no deactivation (reactivity decrease) is produced in this short time interval. On the other hand, when the inorganics are removed by acid treatment, a twofold decrease in reactivity is observed when the pyrolysis residence time (at 1275 K) is increased from 0.3 s to 1.8 s [3]. This deactivation was correlated with a decrease in the concentration of carbon active sites, measured by oxygen chemisorption in the absence of gasification. The gasification behavior of the Rockwell char is very similar to that of the demineralized lignite char, both in the absolute values of their reactivity and the dependence on pyrolysis conditions. Thus, its observed deactivation is also expected to be due to a decrease in its concentration of carbon active sites.

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TABLE 1

Representative operating conditions for selected coal conversion processes with high yields of residual char

| Process	Heating rate (K/s)	Temperature (K)	Residence time	Pressure (MPa)	Atmosphere	Parent coal	Reactor type
Occidental (Flash pyrolysis)	10^4	875—1075	1—2 s	0.1	Recycled combustion gases	Wyoming Monarch subbituminous	Entrained flow
TOSCOAL (Pyrolysis)	10^2	800	15—30 min	0.1	Pyrolysis products	Utah bituminous	Externally heated moving bed
BIGAS (Gasification)	10^5	1375	3 s	5	Char combustion gases	Montana Rosebud subbituminous	Two-stage entrained flow
COED (Pyrolysis)	10^3	610—1175	2 h	0.1	Combustion gases and steam	Pittsburgh bituminous	Four-stage fluidized bed
Rockwell (Hydrogasification)	3×10^5	1175—1275	0.5—2.5 s	0.7	H_2, O_2, H_2O	Kentucky #9 bituminous	Entrained flow
Rockwell (Hydroliquefaction)	3×10^5	1175—1275	60 ms 600 ms	0.7	H_2, H_2O	Kentucky #9 bituminous	Entrained flow
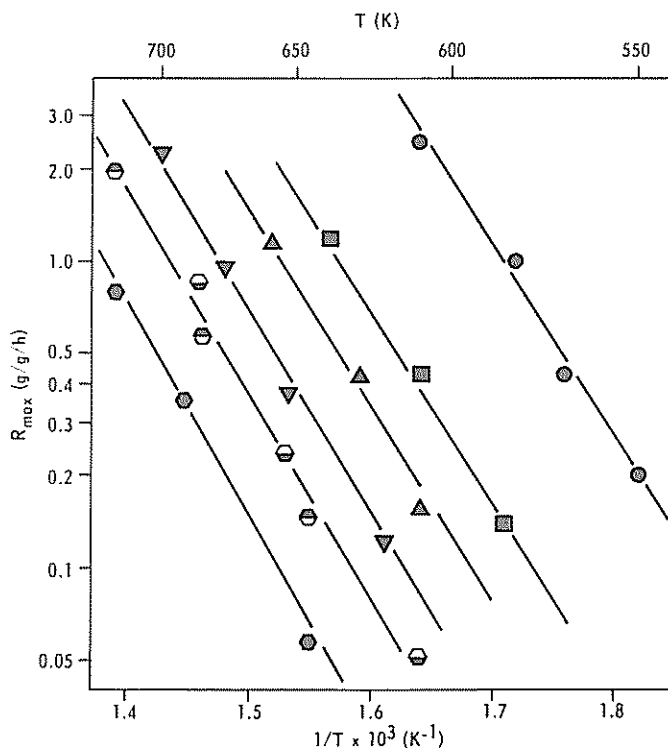
Fig. 1. Reactivities in 0.1 MPa air of chars obtained as residues in selected coal conversion processes: o Occidental; ■ TOSCOAL; ▲ BIGAS; ▼ COED; ○ Rockwell (Hydrogasification); ◐ Rockwell (Hydroliquefaction, residence time = 60 ms); ● Rockwell (Hydroliquefaction, residence time = 600 ms).

At the other extreme, the reactivity of the Occidental subbituminous char is comparable to that of the short-residence-time raw and Ca-exchanged lignite chars [6]. This is what one would predict on the basis of the expected similarity in the composition and dispersion of their inorganic constituents (principally cations exchanged on the carboxyl groups). In Ca-exchanged lignite chars, turnover frequencies were obtained on the basis of the surface area of CaO, measured by X-ray diffraction line broadening [4].

The reactivity of the BIGAS subbituminous char is lower than that of the Occidental char by a factor of about fourteen. This is again what one would predict, based on the more severe heat-treatment conditions of the BIGAS process (see Table 1) and in accordance with the behavior of raw and Ca-exchanged lignite chars [4, 6]. For example, an increase in pyrolysis temperature from 975 to 1275 K resulted in a ten-fold decrease in the reactivity of raw lignite char.

The TOSCOAL and COED bituminous chars are both seen to be more reactive than the Rockwell bituminous chars. This is also understandable, on the basis of their less severe heat treatment. The TOSCOAL char, being sub-
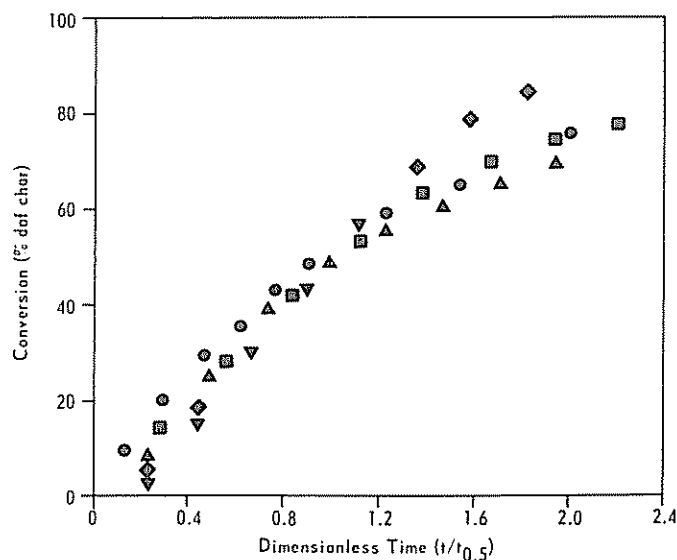
Fig. 2. Normalized TGA plots in 0.1 MPa air for chars obtained as residues in selected coal conversion processes: ● Occidental, T = 585 K ($t_{0.5}$ = 45 min); ■ TOSCOAL, T = 640 K ($t_{0.5}$ = 36 min); ▲ BIGAS, T = 660 K ($t_{0.5}$ = 41 min); ▼ COED, T = 675 K ($t_{0.5}$ = 45 min); ◆ Rockwell (Hydrogasification), T = 685 K ($t_{0.5}$ = 44 min).

jected to the least severe pyrolysis conditions is, indeed, more reactive than a demineralized lignite char prepared under somewhat similar (more severe) conditions (975 K, 1 h). For example, at 600 K, its reactivity is about 0.25 h^{-1}, while that of the demineralized lignite char is about 0.04 h^{-1} [9].

Figure 2 shows the shapes of the conversion vs. time plots for the various chars. It is seen that in the region of 30—60% conversion, all the chars exhibit very similar behavior. However, initially there is a wide variation in behavior, probably reflecting differences in the porous structure of the chars. For example, the Occidental subbituminous char again behaves similarly to the raw and Ca-exchanged lignite chars [9], the initial slope (reactivity) being at the same time the maximum slope. At the other extreme, COED char exhibits a substantial induction period before maximum reactivity is observed. The understanding of these plots in terms of variation of active surface area during reaction still represents a challenge to researchers in this field.

The experimental results presented above show a striking similarity in the gasification behavior of bituminous coal chars and demineralized lignite chars on the one hand, and of subbituminous chars and raw lignite chars on the other. The success of the authors in explaining the gasification behavior of lignite chars on the basis of their active surface area [3—5, 9] and the above mentioned similarity support the usefulness of this fundamental approach to the kinetics of coal char gasification in general. Further development of this approach thus seems to be the most promising avenue of re-

search which will eventually lead to the possibility of reactor design on the basis of rate parameters obtained in the laboratory. In particular, new and complementary methods of measuring catalyst dispersion on the char surface should be formulated. Also, the measurement of the variation of active surface area with conversion is necessary. At the present time, our study has demonstrated that the fundamental concept of active sites, developed in the field of catalysis and carbon gasification, can be successfully used to quantify in a meaningful manner and explain the complex gasification behavior of coal chars.

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