

Fraction estimation and O₂ gasification of solid products from coal pyrolysis in a pressurized drop tube furnace

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Abstract

Coal gasification leaves more or less amounts of solid products, char and soot, the origins and reactivities of which are different from each other. The soot and char is inevitably recovered as a mixture, and this makes it difficult to investigate their reactivities individually as well as separate them from each other. The present study aimed to investigate the reactivity of the soot that had been recovered from a drop-tube reactor (as an experimental simulator of a part of practical entrained-flow type gasifier). A soot/char mixture was immersed in ethanol, and subjected to ultrasonic irradiation to break strong physical interaction between the char and soot, and then emulsion/solid phase separation. This sequence successfully isolated the char and soot particles from each other. The soot/char mass fractions were in agreement roughly with those judged from thermogravimetry for the O₂ gasification of the mixture. The isolated char and soot were subjected individually to the gasification. The results, taken together with that for the mixture, showed a kinetic interaction between the char and soot in the early stage of the gasification, and this was attributed to the presence of catalytic species with the soot. More rapid gasification of the soot than commercially available carbon blacks was at least partly due to such catalysis.

1. Introduction

Coal gasification is a promising technology that is flexibly applicable to power generation and production of synthesis gas. Coal undergoes the primary pyrolysis at temperature over 200°C releasing inorganic gases, light hydrocarbon gases, and tar as fragments of macromolecules. The solid residue from the primary pyrolysis, termed char, experiences gasification in parallel with reforming of tar over

around 600°C (secondary pyrolysis). Although practical gasifiers are operated at temperature well above 1000°C, the char still remains as a byproduct due to its low reactivity with gasifying agent such as CO₂. More problematically, soot is formed from the vapor of aromatics (or those from aromatization of light hydrocarbons such as acetylene), growth in size of aromatic ring systems, nucleation, and then agglomeration. Reactivity of the soot is lower than that of

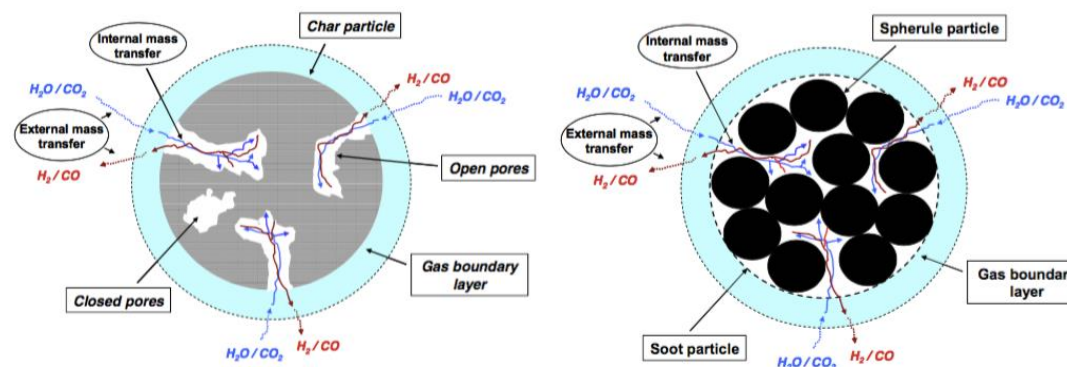


Figure 1. Morphological characteristics of char and soot.

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char when prepared in inert gas.^[1] Difference in the mechanism between the char and soot gasification arises primarily from that in their carbonaceous structure (see **Figure 1**). The char is a porous particle that involves a number of micro- (sizes < 2 nm) and mesopores (< 50 nm). Gasifying agents diffuse into pores and react with active sites as well as the external surface. Whereas, the soot is a non-porous submicron particle that easily agglomerate each other. Instead, the reactant gases can easily diffuse into gaps among soot particles, but the gasification takes place only on the soot surface.

Char and soot, if survive in the gasifier, leave it forming mixed solids. Separation of mixture of char and soot and their quantification have been reported. Miura et al.^[1] quantified the char/soot fractions by temperature-programmed gasification. Umemoto et al.^[2] proposed a laser-diffraction particle size analysis taking notice of size differences between char and soot particles. They also compared the quantification methods including an estimation of char/soot fractions from proximate and ultimate analyses of the parent coal in terms of carbon-based yield of pyrolysis products, showing that all methods were in broad agreement. Varanth et al.^[3] prepared a char/soot suspension in ethanol by ultrasonication, then extracted the relatively stable emulsion of soot particles after the settling, and recovered the precipitated char. This method was then scaled up by Apicella et al.^[4]

This ongoing study will examine fraction of char and soot, which are products of coal pyrolysis in a pressurized drop tube furnace. Then, the reactivities of those solids will be investigated by isothermal O₂ gasification in a thermogravimetric analyzer.

2. Experimental

2.1. Separation of solid products

Pulverized Tandinsky (TS) coal was pyrolyzed at 1200°C in flow of pressurized N₂ (2

MPa) in a pressurized drop tube furnace (PDTF). The particle residence time was estimated as around 3 s.

A 150 mg portion of a char/soot mixture recovered from the PDTF was placed in a 50 ml of glass tube (Tube 1) filled with 40 ml of ethanol. The tube was agitated by ultrasonication for 3min, and was settled for 1–1.5 h. The suspension was then transferred to another tube (Tube 2) leaving the precipitated solid at the bottom of Tube 1. Tube 1 was refilled with ethanol, and both tubes were agitated and settled again. In the same manner, the upper suspension was transferred into the next tube, and a new tube was added up to five. The extraction of the upper emulsion part in the last tube after settling was repeated five times or more until no particle was detected in the upper part of the suspension in Tube 1. The total number of agitation and settling was 10–15. The char and soot were thus recovered from the bottom precipitates and the upper emulsion phases. Ethanol was removed by filtration using a membrane filter of which pore size was 0.45 µm.

This separation method was modified from the previous studies so as to reduce time and ethanol consumption since a major portion of soot was extracted within the first and second cycles. Moreover, incomplete separation was experienced even after 30 repetitions. Although the particle concentration was much higher than that recommended by Varanth et al.^[3], the soot separation from the char was hardly disturbed by rapid aggregation of char/soot particles.

2.2. Thermogravimetric analysis

The gasification of the as-received char/soot mixture, the isolated char and soot was performed in a thermogravimetric analyzer (TGA). The sample was heated at a rate of 25 °C/min to 600°C in atmospheric N₂ flowing at a rate of 700 ml/min temperature increased. The N₂ flow was switched to that of O₂/N₂ with O₂ concentration of 2 vol.%. It was found in preliminary runs for the char/soot mixture that

Table 1. Result of the separation of char and soot.

Char/soot mixture [mg]	Char [mg] (Fraction [%])	Soot [mg] (Fraction [%])	Unseparated (Fraction [%])	Recovered [mg] (Recovery [%])
301 ^[a]	196 (66.0)	82.6 (27.8)	18.6 (6.2)	297 (98.7)

[a] Two separation results were merged.

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every mass release curve had an inflection point (see **Figure 2**), which was arisen probably from the difference in the rate of gasification between the char and soot. The mass fraction of the soot was thus estimated roughly from the gasification of the mixture gasification. However, such a way of estimating the char/soot fraction had no quantitative basis, and the physical separation of them was therefore necessary.

3. Results and discussion

3.1. Estimation of soot fraction

Table 1 presents the result of the char/soot separation. The total mass recovery of the isolated char and soot was as high as 94%, while leaving only 6% of the residue. Assuming that the residue consisted solely of the char (i.e., no soot had been left in the residue), the char and soot fraction were estimated as 72.2% and 27.8%, respectively. These fractions were roughly in good agreement with those estimated from the thermogravimetry of the mixture (see **Figure 1**).

The validity of the char/soot fractions was further examined through the following assumption and calculation^[2]; (1) Oxygen was completely removed (released) from the solid by devolatilization of coal as CO, (2) the char was comprised of fixed carbon and ash, which were determined by proximate analysis, (3) the soot consisted of the other C, i.e., volatile carbon except for that as CO. In the estimation, the fractions of char and soot were considered on the coal carbon basis. Considering that char and soot were highly carbon-rich materials, the estimation was expected to give a reasonable and acceptable result. As seen in **Table 2**, the calculated fractions, 75.3% and 24.7% for the char

and soot, respectively, were in agreement with both those from the physical isolation and thermogravimetry.

However, the char fraction determined by that of the isolated char slightly smaller than those from the thermogravimetry and also shown in **Table 2**. This suggested that a small portion of the char was involved in the isolated soot. This was qualitatively confirmed by observation of the isolated soot by scanning electron microscopy.

3.2. O₂ gasification of char and soot

Derivative thermogravimetry curves of the isolated char and soot during the O₂ gasification are compared in **Figure 3**. X denotes the mass conversion. dX/dt can be expressed by;

$$\frac{dX}{dt} = k_{sp}(1 - X)$$

where, k_{sp} is the specific rate of gasification. The synthesized curve has been drawn by simply assuming that the separated char and soot with a mass ratio of 3:1 were gasified simultaneously and independently according to the results as mentioned above.

It is seen that the isolated char shows slightly higher reactivity than the char/soot mixture. This is in agreement with the fact that the soot produced in inert atmosphere had reactivity lower than that of the char. The reactivity of the mixture seems to be maximized in the early stage of gasification. It is clear that this trend is arisen from that for the char gasification. On the other hand, the dX/dt for the soot

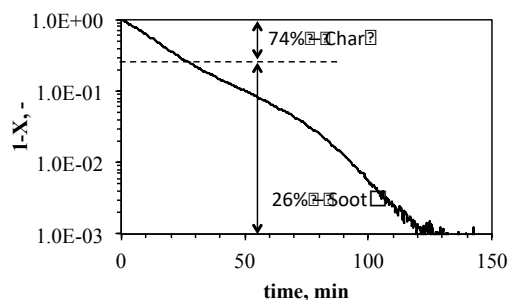


Figure 2. Change in residual mass fraction with time during the gasification char/soot mixture.

Table 2. Composition of Tandinsky coal and estimation of carbon yields in solid products.

Ultimate anal.	wt% (d.a.f. basis)
C	80.70
H	5.16
O	11.37
N	2.39
S	0.38
Proximate anal.	wt% (dry basis)
FC	54.34
VM	35.95
Ash	9.72
Estimation	wt%-C (solid carbon)
Char	75.3
Soot	24.7

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slightly decreases in the early stage, increases very gradually to $X \approx 0.8$, and then decreases later. The initial decrease in the dX/dt would be due to contamination of the soot with a small amount of char, as suggested previously. More importantly, in overall, the dX/dt of the soot is maintained over a wide range of conversion. Such a trend implies the catalysis of metallic species held by the soot.

The synthesized dX/dt slightly but steadily lower than that for the mixture, indicating chemical interaction between the char and soot. Assuming the presence of catalytic species on the soot, the positive synergistic effect of the mixing can be interpreted by solid-to-solid transfer of such species, or otherwise, by that the char and soot (in contact with each other) shared the species at their interface. It seems that the positive synergistic effect diminishes along the gasification and turns even negative. This could be chemical incorporation of the catalytic species (metallic species) with the mineral matter of the char.

In order to confirm catalysis during the soot gasification, a commercial carbon black, Ketjen Black EC-300J, was gasified under the

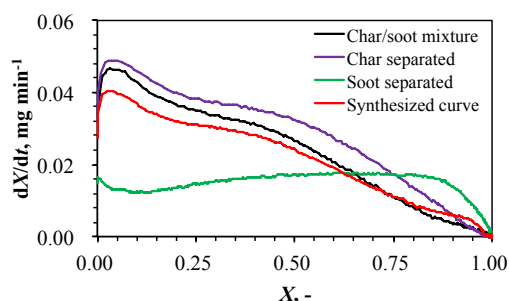


Figure 3. dX/dt profiles for the gasification of char/soot mixture, char, and soot.

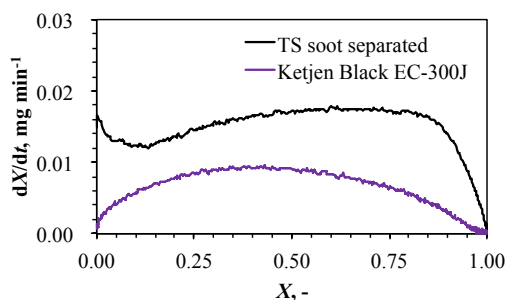


Figure 4. dX/dt profiles for the gasification of the isolated soot and carbon black.

same conditions. **Figure 4** reveals much lower reactivity of the carbon black than that of the soot. The dX/dt for the carbon black changes with X simply showing the surface area increase and then decrease (pore development and col-lapsion). Thus, the clear difference in the dX/dt profile between the carbon black and soot sup-ports the catalysis in the gasification of the lat-ter.

The higher reactivity of the separated soot might also have resulted from the pyrolysis at-mosphere. Senneca et al.^[5] found that soot formed under N_2 atmosphere was a “young soot” based on relatively smaller aggregate size, higher H content, lower structural order of ar-omatic ring systems, more C-O complexes, and higher reactivity than mature soot formed in a CO_2 atmosphere.

4. Conclusion

The char/soot mixture prepared by the py- rolysis of Tandinsky coal in PDTF was sepa- rated into the char and soot, and gasified with O_2 in TGA. The soot particles aggregated over the char surface was successfully isolated from the char by repetitive ultrasonication and set- tling in ethanol. The kinetic analysis revealed chemical interaction between the char and soot in contact. This was, taken together with the kinetics of the soot gasification, explained by the presence of catalytic species, which were held by the soot initially but transferred to the char catalyzing its gasification.

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