GASIFICATON CHARACTERISTICS OF CARBONS PRODUCED UNDER AN ENTRAINED BED GASIFIER CONDITION

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Introduction

Coal gasification to produce gaseous fuel such as CO and H_2 is well known as one of key technologies for utilization of coal. Coal gasification mainly involves two steps: the initial rapid devolatilization of coal to produce char, tar and gases and the subsequent gasification of the char produced. Char gasification, being the slower step, is believed to control the overall conversion process. Therefore, numerous studies have been performed to examine the gasification rate of char. It is, however, known that solid carbon called coke (soot) is formed from the volatiles produced during the initial devolatilization at high temperature above 1000°C. Since the gasification reactivity of the coke is expected to be rather low, it is important to examine if the coke is really formed and to estimate the gasification reactivity of the coke if it is formed.

In this study it was examined if the coke is actually formed at high temperature and high pressure from the equilibrium calculation and experiments using a pressurized drop tube furnace (PDTF). Next, the reactivity of the solid carbons prepared was examined using temperature-programmed reaction (TPR) technique.

Experimental

Coal Sample. The coal used was Bontang coal from Indonesia (C: 78.3, H: 5.4, N: 1.9, O: 14.5 %d.a.f., VM: 42.4, FC: 51.8, Ash: 5.8 W d. b.). It was received as pulverized form, and dried at 108 °C for more than 8 h before use.

Preparation of solid carbons at high temperature and high pressure using a PDTF. Solid carbons were prepared at by using a pressurized drop tube furnace(PDTF) in a nitrogen stream[1]. The coal was rapidly heated to a desired temperature under pressurized condition and the solid carbons and gaseous products produced were collected by a movable water-cooled probe. By changing the axial position of the probe the residence time (τ) of the coal was changed. The gaseous products were analyzed for H_2, CH_4, CO, CO_2 by use of GCs. The carbon yield was estimated from the ash balance. The pyrolysis conditions employed are listed in Table 1. The experimental runs were abbreviated to R-pressure in MPa-temperature in °C/100-residence time in s. The experimental conditions employed for the runs of R-2.1-12-4.3 and R-2.1-14-4.3 are rather close to those in entrained bed gasifier.

A char was also prepared at 1200 °C in a 0.1 MPa of nitrogen atmosphere (τ = 1 min) using a thermobalance under a heating rate of 1500 °C /min for comparison purpose (TG-0.1-12-600).

Table 1 Pyrolysis conditions employed by a PDTF

Run	*P* [MPa]	*T* [℃]	τ [s]	Ultimate analysis[wt%, daf] C	H	N	O(dif.)
TG-0.1-12-600	0.1	1200	60	91.0	0.6	1.1	7.4
R-0.15-12-5.2	0.15	1200	5.2	95.6	0.5	1.4	2.5
R-0.15-14-5.2	0.15	1400	5.2	97.4	0.4	0.8	1.4
R-0.6-12-3.5	0.6	1200	3.5	94.9	0.6	1.6	2.9
R-0.6-14-3.5	0.6	1400	3.5	96.5	0.5	1.4	1.6
R-0.6-14-0.85	0.6	1400	0.85	92.8	0.3	0.7	6.2
R-2.1-12-4.3	2.1	1200	4.3	96.8	0.5	1.2	1.5
R-2.1-14-4.3	2.1	1400	4.3	98.3	0.3	0.6	0.8

Gasification of solid carbon and char. Gasification of solid carbon or char was performed by use of a thermobalance (Shimadzu, TGA-50) under atmospheric pressure using the so-called temperature-programmed reaction (TPR) technique. A very small amount of sample (<0.3 mg) was dispersed in high-grade quartz wool and the sample with the quartz wool was placed on a platinum mesh basket. It was then heated at 10 °C/min from 110 to 1300 ° C in a pure CO_2 flow. The conversion (*X*) vs. temperature (*T*) relation-ships obtained were analyzed to estimate the rate parameters of the samples.

Equilibrium calculation. Equilibrium calculation was made using CHEMKIN Collection III. The products were assumed to be H_2, CH_4, H_2O, CO, CO_2, and C (solid carbon) because the pyrolysis temperatures were very high.

Results and Discussion

Pyrolysis of coal at high temperature and high pressure using a PDTF. Figure 1 compares the experimentally obtained pyrolysis yields with the equilibrium yields at 2.1 MPa for three temperatures. The yields of products are represented by mole fraction. The product yields coincided with the equilibrium calculations above 1200 °C at 2.1 MPa. These results clearly indicate that the equilibrium state is attained immediately at high pressure and the products solely consist of CO, H_2 and solid carbon under the conditions.

Figure 2 compares the experimentally obtained solid carbon yields and calculated ones at 2.1 MPa for different temperatures. The char yield for TG-0.1-12-600 is also shown for comparison. At 1200°C the solid carbon yield obtained at 2.1 MPa was much larger than the char yield at 0.1 MPa. At 0.1 MPa the pyrolysis products contained tar and

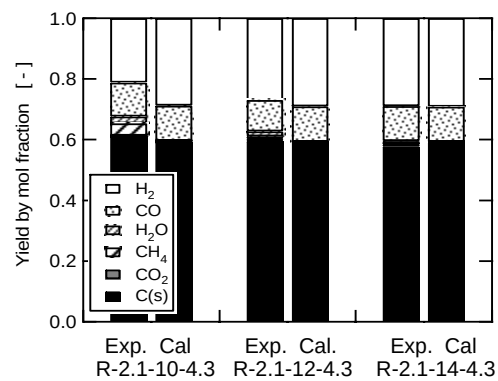


Figure 1. Comparison of experimentally obtained pyrolysis yields and calculated ones.

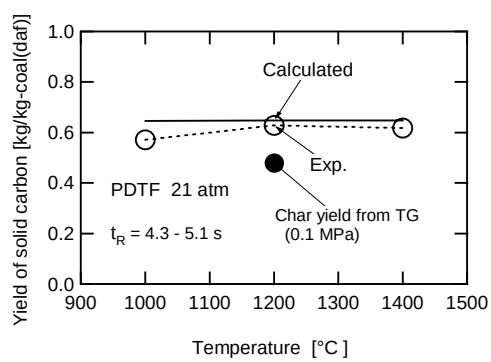
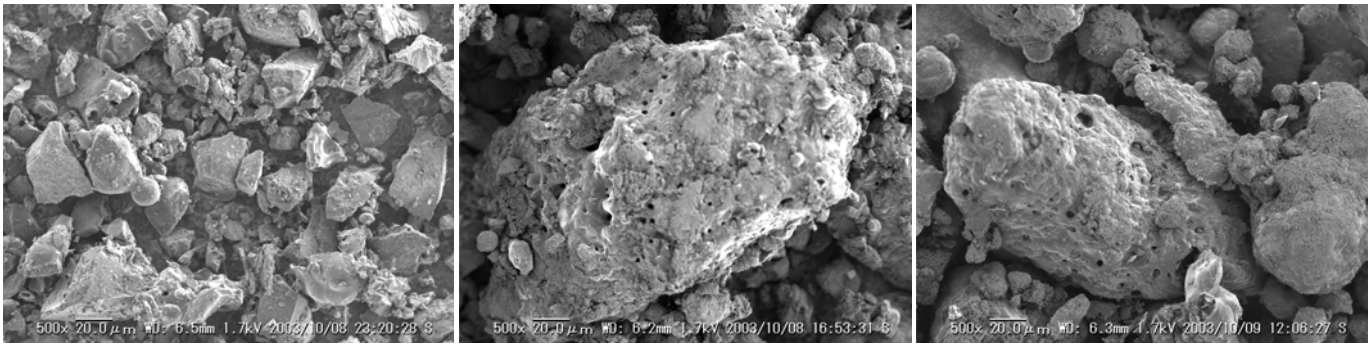


Figure 2. Comparison of experimentally obtained solid carbon yields and calculated ones.



TG-0.1-12-600 (Prepared by TG) R-0.15-12-5.2 (1200 ° C, 0.15MPa) R-2.1-12-4.3 (1200 ° C, 2.1MPa)

Figure 3. SEM images of the char and the solid carbons prepared at 1200 ° C under different pressures.

hydrocarbon gases in addition to the char, CO, and H_2. These results indicate that the solid carbon obtained at 2.1 MPa surely contains char and coke produced from tar components. The ultimate analyses of the char and the solid carbons obtained are also given in Table 1. It is clear that the carbon content increases with the severity of the pyrolysis conditions. The solid carbon prepared under the severest pyrolysis conditions (R-2.1-14-4.3) consisted of 98.3%of carbon.

Figure 3 shows SEM images of the char and the solid carbons prepared at 1200 °C at 0.1, 0.15, and 2.1 MPa. The char obtained at 0.1 MPa using the TG (TG-0.1-12-600) retains the shape and morphology of the raw coal, but the shape and morphology of the solid carbon obtained at 0. 15MPa using the PDTF (R-0.15-12-5.2) are completely different from those of the raw coal. Agglomeration of the solid particles and the deposition of small particles on larger particles are clearly observed, indicating that coal particles were fused and tar components deposited as coke on the fused particles during the pyrolysis. On the other hand, the solid carbon obtained at 2.1 MPa (R-2.1-12-4.3) is judged to consist solely of particles fused during the pyrolysis.

Summarizing the results given above, we can depict the pyrolysis behavior at two extreme conditions as follows. At low pressure and slow heating rate tar and hydrocarbon gases in addition to char and inorganic gases are produced during the early stage of pyrolysis. Those components are finally converted to coke, CO, and H_2 if they are exposed to high temperature. At high pressure and large heating rate, on the other hand, little tar and hydrocarbon gases are produced during the early stage of pyrolysis due to either the suppression of the volatilization of the components or rapid transformation of the components to coke, CO, and H_2 within coal particles. The net difference of the two extreme pyrolysis conditions at equilibrium conditions is that the coke and the char are separated at low pressure and slow heating rate and that the coke are char are both retained in the particles at high pressure and large heating rate. This means that the solid carbons obtained at high pressure using the PDTF consists of char and coke.

Estimation of gasification reactivity of the solid carbon through the TPR experiment. Figure 4 shows the 1-*X vs. T* relationships obtained by the TPR experiments for the solid carbons. Several solid carbons were clearly gasified in two stages, which means that the solid carbons consist of two parts. The more reactive part and the less reactive part were, respectively, judged to be char and coke. The proportion of the coke in the solid carbon (*Y*) and the gasification rate parameters for the two parts were estimated by applying the Bhatia model[2] to the 1st and and 2nd stages by using the technique proposed by Mura et al.[3,4]:

Next, the rate constants at 1200 °C of the 1st and the 2nd stages were estimated using the estimated parameters, and they are shown in Figure 5. The rate constants for the 2nd stage (coke) were smaller than those of the 1st stage by the order of 1. The Y values ranged from 0.4 to 0.6. suggesting that the fraction of coke in the solid carbon is considerably large. Thus the reactivity of the solid carbon produced under an entrained bed condition was characterized.

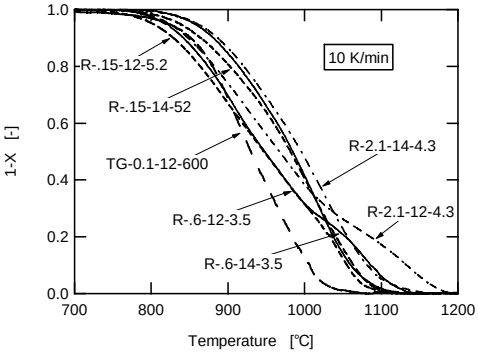


Figure 4. 1-*X* vs. *T* relationships obtained by TPR in an atmospheric CO_2..

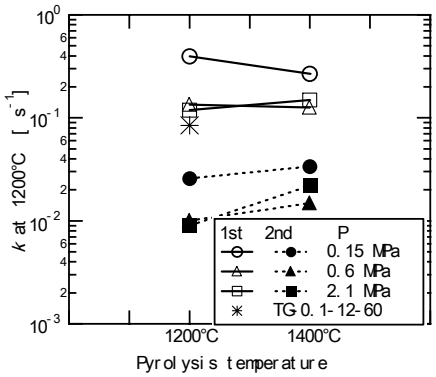


Figure 5. Gasification rate constants at 1200 ° C estimated from the gasification parameters for the 1st and the 2nd stage gasifica-tions.

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