Fuel Processing Technology 159 (2017) 67–75

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Some factors influencing the fluidity of coal blends: Particle size, blend ratio and inherent oxygen species

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ARTICLE INFO

Article history:
Received 10 August 2016
Received in revised form 19 December 2016
Accepted 11 January 2017
Available online xxxx

Keyword:
Caking coal
Non- or slightly-caking coal
Blend coal
Fluidity
Gaseous oxygen containing compounds
Particle size
Blend ratio

ABSTRACT

The fluidity performance of blended coals prepared from caking coal and non- or slightly-caking coal of different particle sizes, and the evolution of gaseous oxygen containing compounds (CO, CO_2 and H_2O) during carbonization are examined using the Gieseler plastometer method, and a flow-type fixed-bed quartz made reactor, respectively. The heating rate and temperature are 3 °C/min and 1000 °C, respectively. The Gieseler fluidity decreases with increasing blend ratio of non- or slightly-caking coal to caking coal. In addition, the fluidity tends to decrease with the decreasing particle size of non- or slightly-caking coal in blended coals. The evolution of CO, CO_2 and H_2O during the carbonization of single coals begins at 200–400 °C, and the main peak of the formation rate appears at 450–700 °C. The amount of gaseous O-containing compounds evolved until 1000 °C from the non- or slightly-caking coals is greater than that of evolved from the caking coal. Additionally, a negative correlation is observed between the amounts of CO, CO_2, and H_2O that evolve up to the initial softening temperature and the maximum fluidity value. The profiles of formation rates of the three gaseous O-containing compounds from the blended coal during carbonization are different with additive average based on the results of single coals. Furthermore, for the blended coal, the starting temperature H_2O evolution measured shifts to higher temperature in comparison with that of calculated based on the results of single coals. Therefore, it is possible that the H_2O produced from non- or slightly-caking coal in blended coal or that the H_2O formation reactions in blended coal during carbonization affects the fluidity performance of the blended coal.

1. Introduction

Caking coal that shows thermoplastic properties during its carbonization is used in the manufacture of metallurgical coke. However, new methods are being developed to use low rank coal and non- or slightly-caking coal as much as possible in the coke manufacturing process because the depletion and appreciating of caking coal are expected in the future. When non- or slightly-caking coals are used in the coke manufacturing process, different methods for the blending of non- or slightly-caking coal and caking coal are utilized. As it is well known, it is very important to use the optimum blending control index for the blending of non- or slightly-caking coal because the thermoplastic performance of coal is one of the factors in determining the coke strength [1,2]. Therefore, thermoplasticity of blended coal is an important theme to produce high quality coke from blended coals containing a majority of non- or slightly-caking coal. Furthermore, for the effective use of a variety of non- or slightly-caking coals, it is essential to better understand the physical and chemical interactions between coals resulting from blended coal samples. In general, the γ-component theory, metaplast theory, transferable hydrogen theory and the continuous self-dissolution model are propounded to help explain the coal thermoplasticity mechanism [3–7]. Non- or slightly-caking coal is considered to have a comparatively high oxygen content, and this is thought to negatively affect its fluidity properties during carbonization [8–11]. According to previous reports, the decomposition/reaction of the hydroxyl- and carboxyl-group generates cross-linking prior to the initial softening temperature of coal, and this affects future thermoplastic performance [8,9]. From a detailed examination of the coal fluidity and evolution of gaseous O-containing compounds in the carbonization process of 10 kinds of caking coal, our research group found that a negative correlation exists between the generation of CO, CO_2, and H_2O that evolved up to the initial softening temperature, and the maximum fluidity value [11]. It is suggested from the results that the O in coal has a negative influence on the coal fluidity. Furthermore, it has been reported that the oxidization of caking coal significantly reduces its fluidity [12]. On the other hand, evaluations of the estimation of blended coal fluidity and the degree of interaction between the blended coals, are being conducted using a Gieseler plastometer, high-temperature *in-situ* ^1H NMR methods and dynamic viscoelastic measurements [13–18]. However, the influence of the particle size of non- or slightly-caking coal on the fluidity of blended coal has not been investigated.

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http://dx.doi.org/10.1016/j.fuproc.2017.01.017
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Furthermore, the effect of O-containing species in blended coal prepared from caking coal, and the different particle sizes of non- or slightly-caking coal on fluidity has not been clearly understood.

Therefore, in the present work, we first investigated the effect of the blend ratio (non- or slightly-caking coal to caking coal) on the fluidity of blended coal, and then examined the influence of the particle size of the non- or slightly-caking coals on the thermoplasticity of the blended coal. In addition, the release behavior of gaseous O-containing compounds (CO, CO_2 and H_2O) during the carbonization of variously seized coals and blended coals was investigated, and the effect of the gaseous O-species on the fluidity of the blended coal was discussed.

2. Experimental

2.1. Coal samples

Three kinds of Australian coals (GA, NC and TA) were used in this study. GA is caking coal, and NC and TA are non- or slightly-caking coals. The particle size of GA was constant at 250–425 μm. On the other hand, NC and TA were ground and sieved to coal particles with size fractions of 53–150, 150–250 and 250–425 μm. The ultimate and proximate analyses are provided in Table 1. The C and O contents of the coals ranged from 82 to 89 and 4–11 mass%-daf, respectively. The blend ratio of NC or TA to GA was varied from 10 to 50 mass%. The fluidity measurements of all samples were carried out using the Gieseler plastometer method (JIS M 8801), and details of this procedure have been previously published [11]. In this study, initial softening temperature, maximum fluidity temperature or resolidification temperature and maximum fluidity value of the samples are expressed as IST, MFT or RST and MF, respectively; samples prepared from blends of NC or TA with GA are expressed as GA-NC or GA-TA, respectively.

2.2. Carbonization

The carbonization experiments were carried out with a flow-type fixed-bed quartz-made reactor, as shown in Fig. S1 in the Supplementary content. Details of the experimental procedure have been previously reported [11]. About 0.50 g of the dried sample was charged into a cell in the reactor, and then the reactor was vacuum pumped. Thereafter, high-purity He (>99.9999%) was introduced at 200 cm^3(STP)/min into the system, including the reactor and tar trap, and the effluent was analyzed using micro gas chromatography (GC) (Agilent, 3000A) with MS-5A and PP-Q columns. This was done to ensure that the remaining air was replaced with He until the N_2 concentration in the reactor's gas outlet decreased below 30 ppmv. Finally, the reactor was heated at 3 °C/min to 1000 °C in a stream of He, and quenched to room temperature. The concentration of CO, CO_2 and H_2O that evolved during the carbonization process were on-line analyzed with a GC and a multigas monitor (Innova) equipped with a photoacoustic infrared detector, at 3 min intervals, to obtain the formation rate curves of these gases. The minimum limits of CO, CO_2 or H_2O detection with GC or a multigas monitor are 5, 5 and 50 ppmv, respectively. The reproducibility was within ±2% for CO and ±3% for CO_2 and H_2O in this study. The cumulative amount of O-containing gases that evolved was calculated by integrating each formation rate curve [11].

Table 1
Analyses of coal samples used in this study.

		Elemental analysis (mass% daf)					Proximate analysis (mass% dry)		
Coal	Particle size (μm)	C	H	N	S	O[a]	Ash	VM[b]	FC[a,c]
GA	250–425	88.4	5.0	2.0	0.51	4.1	10.6	22.7	66.7
NC	250–425	82.9	5.5	2.0	0.60	9.0	8.8	35.1	56.1
	53–150	83.2	5.5	2.0	0.61	8.7	8.4	35.3	56.3
T	250–425	82.0	5.3	1.9	0.43	10.4	10.8	35.0	54.2
	53–150	82.0	5.3	1.9	0.40	10.4	10.8	34.7	54.5

[a] Estimated by difference. [b] Volatile matter. [c] Fixed carbon.

3. Results and discussion

3.1. Influence of the blend of non- or slightly-caking coals with caking coal on the fluidity

Fig. 1 shows the Gieseler fluidity profiles of $\mathrm{GA}_{250–425\ \mu m}$, $\mathrm{NC}_{250–425\ \mu m}$, $\mathrm{TA}_{250–425\ \mu m}$ and blended coals prepared using different blend ratios of $\mathrm{NC}_{250–425\ \mu m}$ or $\mathrm{TA}_{250–425\ \mu m}$ to $\mathrm{GA}_{250–425\ \mu m}$. After softening the $\mathrm{GA}_{250–425\ \mu m}$ at 400 °C, the fluidity profile provided the MF value (560 ddpm) at around 460 °C, and the sample re-solidified at 495 °C. The IST of $\mathrm{NC}_{250–425\ \mu m}$ was at 390 °C, and the MFT and RST were observed at 430 and 460 °C, respectively. The MF value of $\mathrm{NC}_{250–425\ \mu m}$ was 130 ddpm (Fig. 1a). When 15 mass%-$\mathrm{NC}_{250–425\ \mu m}$ was blended to $\mathrm{GA}_{250–425\ \mu m}$, the IST, MFT and RST of the blended coal almost corresponded with those of $\mathrm{GA}_{250–425\ \mu m}$; however, the MF value decreased to 425 ddpm. On the other hand, the MF value dropped to 270 ddpm when 30 mass%-$\mathrm{NC}_{250–425\ \mu m}$ was added to $\mathrm{GA}_{250–425\ \mu m}$, and the MFT and RST shifted to lower-temperatures by 5–10 °C. For a 50 mass%-$\mathrm{NC}_{250–425\ \mu m}$ blended with $\mathrm{GA}_{250–425\ \mu m}$, the IST and MFT, RST shifted to lower temperature by about 10 and 30 °C, in comparison with those of $\mathrm{GA}_{250–425\ \mu m}$, and the MF value decreased considerably to 175 ddpm. When ≥30 or 50 mass%-$\mathrm{NC}_{250–425\ \mu m}$ was blended with $\mathrm{GA}_{250–425\ \mu m}$, the fluidity decreased at around 450 °C (after showing the MF). This temperature almost corresponded with the RST (460 °C) of $\mathrm{NC}_{250–425\ \mu m}$. These results are in accordance with those of previous reports, and can probably be explained by the continuous self-dissolution model [7,17–20]. According to this model, coal has inherent numerous components, from lighter-components (such as chloroform-soluble) to heavier-ones (such as mixed solvent-insoluble). The lighter-soluble (mobile) component forms as result of the thermal relaxation of coal, and contributes to dissolve heavier-components. The resulting heavier-soluble (mobile dissolved by lighter-soluble) component then acts to dissolve subsequent heavier-components, and the dissolution of other heavy components proceeds one after another [7,17–20]. In this study, it is suggested that the mobile components, which are derived from the thermal relaxation of NC, first penetrate into the adjoining GA particles, because the IST (390 °C) of NC is lower than that of GA (400 °C). The inherent GA mobile component is dissolved by the abovementioned mobile component from NC, resulting in a shift of the IST and MFT to lower temperatures. In addition, resolidified-NC is able to capture mobile components of GA as inert ingredients, and it causes RST to shift towards lower temperatures, because the RST (460 °C) of NC is lower than that of GA (490 °C) [7,17–20]. However, for GA-15 mass% $\mathrm{NC}_{250–425\ \mu m}$, the RST was almost the same as that of GA, regardless of the decrease in MF having from to 560 to 425 ddpm. This reason can be explained on the basis of the above-mentioned model [7,17–20]. The extent of decreases MF at GA-15 mass% $\mathrm{NC}_{250–425\ \mu m}$ is smaller than 30 or 50 mass%-NC addition to $\mathrm{GA}_{250–425\ \mu m}$ because the enough mobile components (lighter- or heavier-soluble) exist at around MFT. Therefore, the mobile component is able to dissolve the subsequent heavier components in the range from MFT to RST, resulting in RST at GA-15 mass% $\mathrm{NC}_{250–425\ \mu m}$ may be not almost change.

Fig. 1(b) shows the results of blending $\mathrm{TA}_{250–425\ \mu m}$ with $\mathrm{GA}_{250–425\ \mu m}$, where it is observed that $\mathrm{TA}_{250–425\ \mu m}$ began softening at approximately 410 °C, and had its MF (6 ddpm) at around 430 °C. In addition, $\mathrm{TA}_{250–425\ \mu m}$ re-solidified at 455 °C. The fluidity of $\mathrm{TA}_{250–425\ \mu m}$ was extremely smaller than that of $\mathrm{GA}_{250–425\ \mu m}$ or $\mathrm{NC}_{250–425\ \mu m}$. When 15 mass%-$\mathrm{TA}_{250–425\ \mu m}$ was blended with $\mathrm{GA}_{250–425\ \mu m}$, the MF of $\mathrm{GA}_{250–425\ \mu m}$ dropped from 560 to 425 ddpm. Furthermore, for the 30 mass% blend, the IST, MFT and RST were lowered by about 10 °C, in comparison with those of GA and MF decreased considerably to 190 ddpm. For the 50 mass% blend, IST, MFT and RST decreased by