



Research article

Effects of kaolinite addition on the thermoplastic behaviour of coking coal during low temperature pyrolysis

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ABSTRACT

The presence of kaolinite as mineral in coal may significantly influence coking properties of coal, therefore affects quality of coke that is produced from such coals. In this paper, the effect of kaolinite addition on pyrolysis behaviour of coal was examined by blending kaolinite with a medium rank, high vitrinite, low ash coal. Thermoplasticity of coal was characterised by using a Gieseler Plastometer. Char and tar samples were collected through pyrolysis at 450 °C in a Gray-King apparatus. The functional groups of the char samples were measured using FT-IR spectroscopy, while tar compositions were characterised using GC/MS. The results indicated that under the test conditions, addition of up to 5 wt% of kaolinite could increase the coal fluidity, attributed to the decrease in CH₃/CH₂ ratio in the residual char. The proportion of C=O/C=C bonds affected the plastic range. Furthermore, the results showed that kaolinite addition suppresses the evolution of low molecular compounds in tar phase. This study provides useful information for optimising coal blending in cokemaking industry.

1. Introduction

Understanding thermoplastic phenomenon during coal carbonisation is critical for determining coke quality in cokemaking process. The development of thermoplasticity during coal pyrolysis is a complex physiochemical phenomenon, which involves a series of chemical and physical reactions including chemical changes in macromolecular structure, and physical changes such as gas pressure generation and subsequent porosity evolution [1].

Coal rank and maceral compositions are critical when considering the thermoplastic properties of coals. Generally, medium rank coals (volatile matter ~25–35%) show greater caking tendency [2]. Within that range, the maximum fluidity and plastic range increase for higher rank coal [3]. For a given rank, fluidity increases with the total reactive macerals of coal depending on the rank range. However, in some cases, coals of similar ranks and maceral compositions may display significant differences in coal fluidity [4,5].

Given the importance of thermoplastic property of coal, various theories have been proposed to explain the thermoplastic phenomena. The role of ‘metaplast’ was highlighted by van Krevelen [6], according to which, metaplast has a low molecular weight and becomes fluid upon

heating, contributing to the development of thermoplasticity. It is also reported that the transferrable hydrogen species of coal plays an important role. It can stabilize radical fragments splitting from bond cleavage and transform them into ‘solvating’ species [7,8]. Ouchi et al. also described that the amount of the inherent solvent-soluble materials in coal (γ -compounds) is critical, as these materials will melt first and then dissolve the compounds of higher molecular weights so that the whole coal finally shows plasticity [9,10].

In previous studies, strong correlations were found between observed plastic phenomena and molecular transformations that take place during the early stages of carbonisation [11–14]. For example, Ouchi et al. stated that the lower molecular weight material in coal was responsible for the higher fluidity due to the possibility of greater solvent extractability [11]. Clemens et al. reported that oxidation results in a loss of coal plasticity and that the blending a fraction of solvent-soluble coal and/or polyaromatic hydrocarbons with the oxidised coal helps restoring the coal plasticity [12]. Kiden et al. observed the correlation between the concentration of methylene groups that link two aromatic moieties and the maximum fluidity [13]. The relative intensity of methylene groups (–CH₂) in the aliphatic chain was found to decrease with increasing temperature [1]. Recently, Fernández et al.

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highlighted the importance of a higher degree of aromatic condensation in enhancing coal plasticity [14].

In addition to molecular transformations, the presence or addition of some minerals may also influence coal fluidity [15–20]. For example, blending 1 wt% of quartz and kaolinite with coal resulted in a minor increase in the maximum fluidity value [15]. 5–20 wt% of non-porous silica (SiO_2) can reduce the maximum swelling without any notable changes in the fluidity temperatures including plastic range [16]. Iron oxides such as hematite (Fe_2O_3) and magnetite (Fe_3O_4) as well as sulphur can decrease the maximum fluidity [15,17]. In general, addition of alkali species largely will have an adverse effect on fluidity, with 5 wt % of sodium carbonate decreasing the coal fluidity significantly by up to 90% and decreasing the plastic temperature range without changing the maximum fluidity temperature [19]. Addition of potassium carbonate (K_2CO_3) and potassium hydroxide (KOH) each showed a strong effect on coal swelling at low pressures (< 1.0 MPa); however, potassium chloride (KCl) showed little effect as it does not decompose at the pyrolysis temperature [16]. In a recent study, kaolinite-rich coals were shown to exhibit a large plastic range [20]. One can expect that kaolinite may affect, to some extent, the thermoplastic behaviour of coal during pyrolysis. However, understanding of kaolinite addition on thermoplasticity during coal pyrolysis has not been well studied in the past.

In this paper, the effect of kaolinite addition on coal pyrolysis is studied. The changes in molecular compositions of tars and residual chars are studied as a function of varying kaolinite addition in coal. Several correlations are proposed for describing the evolution of thermoplasticity of coal due to kaolinite addition.

2. Experimental

2.1. Sample selection

A medium rank coal of high vitrinite, medium fluidity and low ash content was selected in this study. The coal was crushed and sieved through sieves of 0.4 mm and 0.125 mm sizes to obtain coal sample for fluidity and pyrolysis tests. Prior to the experiments, the crushed and sieved samples were kept in sealed bags in nitrogen to prevent oxidation. A commercial grade kaolinite reagent was crushed and sieved particle sizes < 30 μm as kaolinite samples. The chemical properties of coal and kaolinite samples were measured as per Chinese Standards (GB/T 212–2008; GB/T 1574–2007; GB/T 8899–1998). They are summarised in Table 1.

The fluidity of coals was measured using a Gieseler Plastometer along with Chinese standard (GB/T 25213–2010). Test samples were prepared by mixing of 2, 5 and 10 wt% kaolinite with coal samples. The plastic temperature range (PR) of each sample was obtained by determining the difference between the solidification temperature (ST) and the initial softening temperature (IST). The maximum fluidity temperature (MFT) was also determined, and it corresponds to maximum fluidity (MF) which is expressed as dial divisions per minute (ddpm). The fluidity results are summarised in Table 2.

The thermal behaviour of the coal and blends was investigated by thermogravimetric analysis (TGA) using STA 449 F3 Netzsch instrument. Before the tests, the blends were prepared by weighing and mixing the exact amounts of coal and kaolinite to ensure that the sample was representative. The blend was mixed mechanically for a few minutes until it became homogeneous. Approximately 10 mg of sample with a particle size of < 0.125 mm was placed in the sample cell. The samples were heated from room temperature to 1000 °C at a rate of 3 °C/min. A nitrogen flow of 100 ml/min was used to purge the volatile products. The derivative thermogravimetric (DTG) curve was calculated from the weight loss curve obtained from thermogravimetry, kaolinite mass was subtracted from the DTG curves of coal blends. Tmax, which is the temperature of maximum volatile matter released, was derived from the DTG curve.

Table 1
Chemical properties of coal and kaolinite.

	Coal	Kaolinite
Proximate analysis (%)		
Moisture, ad	0.86	1.42
Ash yield, db	4.04	87.07
Volatile, db	26.16	12.93
Fixed carbon, db	69.80	–
Ultimate analysis (db%)		
Carbon	80.10	–
Hydrogen	4.92	1.37
Nitrogen	1.69	0.02
Sulphur	0.66	–
Oxygen	8.58	11.54
Oxides analysis (wt%)		
SiO_2	52.74	44.81
Al_2O_3	14.30	36.88
Fe_2O_3	9.35	0.52
CaO	8.95	0.41
MgO	7.68	0.16
Na_2O	1.94	–
K_2O	1.32	–
TiO_2	1.11	0.60
SO_3	2.07	–
P_2O_5	0.55	–
Petrology data (%)		
Rv,max	1.18	–
Vitrinite	97.20	–
Inertinite	1.70	–
Liptinite	0.00	–
Mineral	1.10	–

Table 2
Parameters derived from the Gieseler test on coal and its blends with varying kaolinite contents.

Kaolinite (wt%)	MF (ddpm)	IST (°C)	MFT (°C)	ST (°C)	PR (°C)
0	602	411	455	495	84
1	685	410	455	496	86
2	895	410	453	498	88
5	740	411	456	496	85
10	208	418	457	487	69

2.2. Low temperature pyrolysis experiments

The char and tar samples were prepared through a low temperature pyrolysis test in a Gray-King Assembly. 10 g coal specimen was placed in a quartz tube which was located in a horizontal electric furnace. The specimens were each heated at an identical heating rate of 3 °C/min, under standard Gieseler Plastometer test conditions, to a target temperature of 450 °C which corresponds to the maximum fluidity temperature. The volatiles released from the samples were continuously passed through a cooling trap and were condensed as tar in a glass bottle enclosed in an ice bath. After the target temperature is reached, the furnace power was switched off. Then the residual solid char was removed from the quartz tube after half an hour. The chemical compositions of tar and char samples were analysed by GC/MS and FTIR spectroscopy, respectively.

2.3. Char characterisation

The functional groups of char samples were analysed using a Thermo Fisher Nicolet IS5 mid-FTIR spectrometer. To prepare the specimen, the char raw materials are ground with KBr content 1:200 in mass ratio and then compacted into a pellet. Prior to FTIR measurements, a reference spectrum was obtained from a pure KBr pellet. The spectra were obtained with 16 scans at a resolution of 4 cm^{-1} , and the tests were repeated three times to get the average data. The spectra

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