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Full Length Article

Structural transformation of fluid phase extracted from coal matrix during thermoplastic stage of coal pyrolysis

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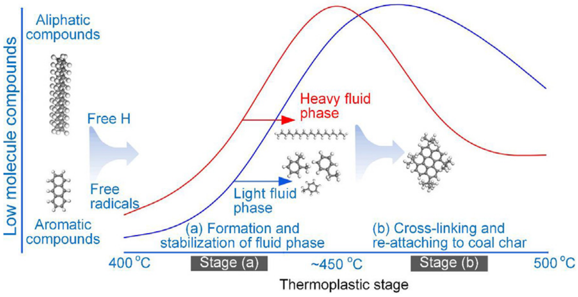
GRAPHICAL ABSTRACT



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ABSTRACT

Two-stage solvent extraction, involving acetone (light extraction) and tetrahydrofuran (heavy extraction), was used to obtain materials from the fluid component of the coal matrix during the thermoplastic stage of pyrolysis. These extracted materials were characterized using Laser desorption ionization time of flight mass spectrometry, Gas chromatography-mass spectrometer, ^{1}H nuclear magnetic resonance and Fourier transform infrared spectroscopy. After identifying the different chemical compounds using the type difference technique, their structural transformation behaviour was considered. Results show that the molecular weight distribution of extracted materials was within 576 Da. Fluid phase obtained from the extract contained aromatic (benzene with alkyl) and aliphatic (long-chain unbranched alkanes) components. The quantity of these two materials increased as pyrolysis temperature increased from 400 to ~450 °C, and then decreased with further increases in temperature from 450 to 500 °C. The overall structural transformation of the fluid phase in thermoplastic stage could be divided into two stages: (a) formation and stabilization of the fluid phase, and (b) the cross-linking and re-attaching of the fluid phase to coal char. In the temperature range of 400 to ~450 °C, the level of both light and heavy fluid phases increased because of the combination of free radicals with hydrogen formed from the cracking of the coal matrix – resulting in shortening of the aliphatic chain length and improving generation of hydrocarbon in the extract. At higher temperatures, the cross-linking and preferential re-attaching of materials to the coal char caused a decrease in the fluid phase level. In turn, this resulted in the lengthening of the aliphatic chains, which weakened their hydrocarbon-generating potential. These two stages explain the transient

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behaviour of the fluid phase generated in the thermoplastic stage, and contribute toward a better understanding of the softening and solidification behavior of coal during coking.

1. Introduction

In processes such as coking, liquefaction and gasification, the thermal conversion of coal is influenced by the what happens during the thermoplastic stage. To improve the efficient utilization of coal [1,2], an understanding of the evolution in chemical structure during this stage, especially the thermochemical transformation mechanisms, is a necessary. Coal becomes thermoplastic when it has transformed into a complex macromolecular structure with several low molecular components. Some of these low molecular materials, regarded as a fluid phase, is the fundamental contributor to its thermoplastic behavior. Not surprisingly, interest in understanding the fluid phase has gained worldwide attention because of its influence on the coal conversion processes, in particular in cokemaking.

Gieseler plastometry and dilation [3] are very widely used to determine the suitability of coals for cokemaking. These two parameters provide information on the plastic properties of coals, which are, in turn, dependent on the properties of the formed fluid phase. High maximum fluidity values and dilation indices indicate the generation of higher amounts of fluid phase in coal. Recently, Small-amplitude oscillatory shear (SAOS) rheometry was used to monitor the viscoelastic properties of coal. Results indicate that both the minimum complex viscosity and the maximum concentration of fluid hydrogen were dependent on the maximum mobility of the fluid phase [4,5]. A more recent study [6] suggests that the fluid phase is associated with the accumulation of a critical amount of polycyclic aromatic fragments. There is also a view that molecular hydrogen sourced from hydroaromatic structures (to form complete aromatic rings) contributes significantly to the structure of the fluid phase [7]. Clearly, the fluid phase has a very complicated composition and the variations in local composition are not insignificant. For this reason, the relationship between the structure of the formed fluid phase and softening and resolidification behaviour in thermoplastic stage is a very complex topic. This work was initiated with the view to provide a greater understanding of the structural transformation of the fluid phase during the thermoplastic stage.

In coal pyrolysis, solvent extraction has been widely used to remove the fluid phase. In early studies, pyridine has been used as a solvent to extract the fluid phase and correlations between Gieseler fluidity and the pyridine extraction yield have been established. This suggests that the pyridine-extractable materials from bituminous coal are relatively small molecules which, on heating, plasticized readily and contributed significantly to the measured fluidity value [8]. However, after pyridine extraction, the residue left still exhibit liquid properties and this suggests that not all the fluid materials generated by thermal treatment have been removed. For this reason, many researchers are of the view that pyridine is not an ideal solvent for fluid phase extraction [9]. More recent studies have shown that a carbon disulfide/N-methyl-2-pyrrolidinone mixed solvent (CS_2/NMP, 1:1 v/v) has the ability to extract a larger amount of the solvent-soluble components that greatly influence coking properties, such as fluidity [10]. The two solvents (CS_2 and NMP) had a synergistic effect on the extraction process, removing more fluid phase compounds compared pyridine [11–13]. In addition, 1-methylnaphthalene mixed with NMP and/or methanol could dissociate the strong formed cross-links, resulting in strong thermal dissolution behaviors from 300 to 360 °C [14]. More recent extraction studies have used tetrahydrofuran (THF), a polar aprotic solvent [15–19]. It appears that the molecular weight distribution of THF-soluble extracts were subject to extraction conditions. However, a combination of the needle penetration test and slurry models suggests that this type of solvent would not be effectively extract all the chemical components of the fluid phase [20]. Regardless of the solvents used, it is not possible to confirm with certainty that all extracted materials have originated from the fluid phase. In conclusion, all possible solvent extraction and analytical methods should be operated to obtain the maximum amount of fluid phase compounds and reducing the contribution from other sources.

This work involved two-stage extraction, using acetone and THF as solvents. The aim was to obtain a wide range of light and heavy compounds from the coal matrix in the thermoplastic stage. The extracted samples were characterized using Laser desorption ionization time of flight mass spectrometry (LDI-TOF-MS), Gas chromatography- mass spectrometer (GC–MS), ^{1}H nuclear magnetic resonance (^{1}H NMR) and Fourier transform infrared spectroscopy (FT-IR). The different types of chemical compounds in the extract were determined and the structural transformation of the materials was then studied.

2. Experimental

2.1. Sample preparation

A coal sample (Zhujiao Coal, ZC, from An Steel, northeast of China) was crushed to 0.150 and 0.425 mm. The basic property of the sample, as characterized by Chinese Standard Methods GB/T 212-2008 [21], GB/T 31391-2015 [22], GB/T 6948-2008 [23], GB/T 8899-2013 [24], GB/T 479-2000 [25], GB/T 5447-2014 [26], GB/T 25213-2010 [27], is summarized in Table 1. The sample was de-mineralized before the pyrolysis experiments to avoid the influences of minerals on the structure transformation of fluid phase. Approximately 500 g coal sample was dispersed in the 3000 mL HCl (36.5%) for 2 h at 50 °C. The

Table 1
Basic property analysis of the coal sample.

Coal	ZC
Proximate Analysis (wt.%)	
Moisture, air dry	2.30
Ash, dry	7.53
Volatile, dry	20.57
Fixed carbon, dry	71.90
Ultimate analysis (air dry, wt.%)	
Carbon	81.35
Hydrogen	4.58
Nitrogen	1.45
Sulphur	0.37
Oxygen	4.73
Petrology data (%)	
Vitrinite reflectance, max	1.23
Vitrinite	64.30
Inertinite	25.90
Liptinite	1.40
Minerals	8.40
Gelatinous layer index (mm)	
Maximum thickness of plastic layer	7.00
Maximum volume shrinkage of plastic layer	45.00
Caking index (%)	13.00
Thermoplasticity (demineralized)	
Thermoplastic stage (°C)	423–495
Initial softening temperature (°C)	423
Maximum fluidity (ddpm)	192
Maximum fluidity temperature (°C)	453
Solidification temperature (°C)	495
Plastic range (°C)	72