



Novel carbon-rich additives preparation by degradative solvent extraction of biomass wastes for coke-making



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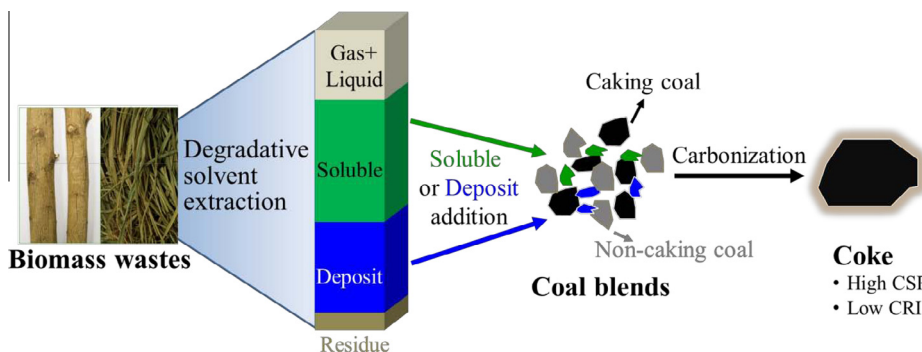
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HIGHLIGHTS

- Soluble and Deposit were produced by degradative solvent extraction of biomass.
- Soluble and Deposit had good thermoplastic properties.
- Adding Soluble and Deposit into coke-making coal improved its thermoplastic properties.
- The addition of Deposit or Soluble markedly enhanced the coke quality.
- Soluble and Deposit were proved to be good additives for coke-making.

GRAPHICAL ABSTRACT

Using Soluble and Deposit prepared from biomass as additives for cokemaking.



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ABSTRACT

In this work, two extracts (Soluble and Deposit) were produced by degradative solvent extraction of biomass wastes from 250 to 350 °C. The feasibilities of using Soluble and Deposit as additives for coke-making were investigated for the first time. The Soluble and Deposit, having significantly higher carbon content, lower oxygen content and extremely lower ash content than raw biomasses. All Solubles and most of Deposits can melt completely at the temperature ranged from 80 to 120 °C and 140 to 180 °C, respectively. The additions of Soluble or Deposit into the coke-making coal significantly improved their thermoplastic properties with as high as 9 °C increase of the plastic range. Furthermore, the addition of Deposit or Soluble also markedly enhanced the coke quality through increasing coke strength after reaction (CSR) and reducing coke reactivity index (CRI). Therefore, the Soluble and Deposit were proved to be good additives for coke-making.

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1. Introduction

Coke is an essential industrial material in iron and steel industry, which acts as the important roles of carbon skeleton, main fuel, reducing agent in blast furnace (Hutny et al., 1991). The coking

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coals for coke production have scarce reserves and much higher price than steam coals used for electricity generation, because of their special physical and chemical properties. Due to the rapid consumption and increasingly high price of prime coking coals in past decades, coal blending is a common practice in coke-manufacturing industry to lower the cost of coke-making (Castro Díaz et al., 2012; Shui et al., 2015). However, the addition of non-caking coals into coking coal blends usually causes an obvious reduction of the thermoplastic properties of coal blends and the quality of subsequently produced coke. For these reasons, various carbon-containing materials, such as pitch, tyre recycling residue, plastics, biochar and petroleum coke, have been used as additives in coke-making (Du et al., 2014; Fernández et al., 2009; Melendi et al., 2011; Pis et al., 2002). However, these additives usually contain high sulfur content, emit high amount of pollutants or result in a certain reduction of the coke quality. Therefore, it is of great importance to find or produce substituted additives for coke-making.

The authors have recently presented a degradative solvent extraction method to upgrade and convert various types of biomass wastes into carbon-rich products (Li et al., 2012, 2015; Wannapeera et al., 2012; Zhu et al., 2015). This method treats the biomass wastes in a non-polar solvent below 350 °C under an inert atmosphere. The products consist of an unextractable fraction (termed Residue), high molecular weight fraction (Deposit) which is extractable at extraction temperature but precipitated at room temperature, and low molecular weight fraction (Soluble) which is also extractable at extraction temperature and still soluble in the solvent at room temperature. Soluble and Deposit have carbon content of as high as 80.1–89.5%, and have oxygen content of as low as 7.3–15.4%. They can melt at around 80–250 °C, like pitch. In addition, the both products are almost free from water and ash, and have the sulfur content of all most null since they are biomass-derived products. In view of their advantageous properties, it seems highly potential for Soluble and Deposit to be used as additives for coke-making. The Soluble and Deposit, as biomass-derived additives, also have the advantage of reducing the CO₂ emission over other additives derived from fossil fuels such as coal and petroleum, because of the carbon-neutral and zero net carbon dioxide emission characteristics of biomass (Chen et al., 2012; Jeong et al., 2014).

Consequently, in this study, the feasibilities of using these two extracts (Soluble and Deposit) as additives for coke-making were examined for the first time. The Soluble and Deposit were prepared from two typical biomasses by degradative solvent extraction at different temperatures and then characterized in detail. Considering the importance of thermoplastic properties of raw coals for final coke properties, the influences of Soluble and Deposit additions on thermoplastic properties of coal were investigated. The effect of the additions of Soluble and Deposit on the coke qualities were finally studied and discussed.

2. Methods

2.1. Degradative solvent extraction procedure

Two typical biomass wastes, a rice straw (RS) and a fir sawdust (SD) from China, were used as the raw biomass materials. The ultimate and proximate analyses of RS and SD are presented in Table 1. 1-Methylnaphthalene (1-MN), a non-hydrogen donor and non-polar solvent, was used as the solvent for the extraction. The schematic diagram of the batch autoclave and detailed experimental procedure were already described in our previous studies (Zhu et al., 2016, 2015). Briefly, 30 g of biomass (air-dry basis) and around 300 mL of 1-MN were charged into the autoclave extractor.

A stainless filter (0.5 µm opening) connecting the autoclave and the reservoir was equipped at the bottom of the autoclave. After sufficiently purging by N₂ several times, the extractor was sealed with N₂ of 0.2 MPa and heated to the desired temperature (250, 300, 350 °C) at the heating rate of 5 °C/min, and then held at the desired temperature for 30 min. Then, the valve below the filter was immediately opened to transfer the extracts along with the solvent to the reservoir, realizing the in-situ separation of the Residue from the extracts. The reservoir and the autoclave extractor were cooled down by circulating cooling water at ambient temperature and an electric fan, respectively. A fraction of the extracts which was extractable at extraction temperature but precipitated in the reservoir at room temperature was termed as Deposit. The other fraction of the extracts which was also extractable at extraction temperature and still soluble in the solvent at room temperature was termed as Soluble. Soluble was separated from Deposit by filtration. The solid Soluble was obtained by remove the solvent in vacuum rotary evaporator at around 150 °C. Subsequently, Residue, Soluble and Deposit were further dried in a vacuum drying oven at 150 °C for 5–8 h to sufficiently remove the residual 1-MN. The gaseous products (Gas) were gathered in a gas bag and analyzed quantitatively by a gas chromatograph (Micro GC 3000, Agilent). The yields of Gas, Soluble, Deposit and Residue were estimated by measuring their weights. The yield of Liquid was then obtained by mass balance. Each extraction experiment was carried out at least three times, and the average value was reported with the experimental errors within 3%.

2.2. Product analyses

The ultimate analysis was performed by an elemental analyzer (CHN EL-2, Vario). The proximate analysis was carried out using a muffle furnace according to GB/T212-2008 standard procedure. Thermal decomposition behaviors of solid products were determined using a thermogravimetric (TG) analyzer (Diamond TG/DTA, PerkinElmer). About 10 mg sample was heated to 900 °C at a heating rate of 10 K/min in a flow of 80 mL/min pure nitrogen. The FTIR spectra of raw biomasses and solid products were recorded using a Bruker VERTEX-70 FTIR spectrometer ranging from 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹. The softening/melting behaviors were estimated by using a thermomechanical analyzer (TMA Q400EM, TA Instruments). 150 mg of the sample was compressed under 10 MPa at room temperature into a pellet (8 mm in diameter and around 2.5 mm height) using an electric tablet machine (SDY-20, China). The displacement of the sample pellet was continuously monitored when the pellet was heated up at 10 K/min under a load of 0.098 N in nitrogen stream in TMA.

2.3. Gieseler test

Gieseler plastometry has long been a widely used method for evaluating coal or coal blends thermoplasticity (Clemens and Matheson, 1995). In this study, a representative gas coal (GC, from China) with 36.74 wt% volatile matter (daf basis) was employed as the base coal of the blends, which contains 77.28 wt% of carbon, 1.68 wt% of hydrogen, 3.64 wt% of nitrogen and 17.40 wt% of oxygen (dry basis). The proportion of the Soluble or Deposit added to GC was 2.0 wt%. The thermoplastic properties of the raw GC and blends were estimated in a constant-torque Gieseler plastometer (PL-2006A, China), according to the GB/T 25213-2010 standard procedure. The samples of 0.5 g were heated up from 300 °C to 550 °C at a heating rate of 3 °C/min. The parameters reflecting the thermoplastic properties of the coal or blends were obtained from the test: (1) T_s: softening temperature; (2) T_f: the temperature corresponding to maximum fluidity; (3) T_r: resolidification

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