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

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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.

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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.

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
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; Wannapaera 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 addition 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-Methylphenanthrene (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 also 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 TGA 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) Tg: softening temperature; (2) Tp: the temperature corresponding to maximum fluidity; (3) Tf: resolidification
temperature; (4) plastic range ($P_t$); $T_r$ – $T_t$; (5) MF: maximum fluidity (ddpm).

2.4. Carbonization experiments and crucible coking assessment

The carbonization experiments were carried out in a laboratory-scale crucible coking oven. The raw coal blends employed in this study was an industrial coal blends provided by an iron and steel company from China, which was mainly composed of a coking coal, a gas coal, a fat coal and a lean coal. The proportion of the Soluble or Deposit added to coal blends was 2 wt%.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ultimate analysis (wt.%, daf)</th>
<th>Proximate analysis (wt.%,db)</th>
<th>Atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>RS-250</td>
<td>Soluble</td>
<td>49.01</td>
<td>5.54</td>
</tr>
<tr>
<td></td>
<td>Deposit</td>
<td>67.33</td>
<td>6.11</td>
</tr>
<tr>
<td>RS-300</td>
<td>Soluble</td>
<td>75.78</td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td>Deposit</td>
<td>73.29</td>
<td>5.91</td>
</tr>
<tr>
<td>RS-350</td>
<td>Soluble</td>
<td>78.80</td>
<td>6.73</td>
</tr>
<tr>
<td></td>
<td>Deposit</td>
<td>79.68</td>
<td>6.23</td>
</tr>
<tr>
<td>SD-250</td>
<td>Soluble</td>
<td>72.76</td>
<td>6.97</td>
</tr>
<tr>
<td></td>
<td>Deposit</td>
<td>69.45</td>
<td>6.06</td>
</tr>
<tr>
<td>SD-300</td>
<td>Soluble</td>
<td>75.97</td>
<td>6.46</td>
</tr>
<tr>
<td></td>
<td>Deposit</td>
<td>74.93</td>
<td>5.27</td>
</tr>
<tr>
<td>SD-350</td>
<td>Soluble</td>
<td>76.60</td>
<td>6.17</td>
</tr>
<tr>
<td></td>
<td>Deposit</td>
<td>75.86</td>
<td>5.52</td>
</tr>
</tbody>
</table>

The carbonization experiments were carried out in a laboratory-scale crucible coking oven. The raw coal blends employed in this study was an industrial coal blends provided by an iron and steel company from China, which was mainly composed of a coking coal, a gas coal, a fat coal and a lean coal. The proportion of the Soluble or Deposit added to coal blends was 2 wt%. On each run, 100 g of raw coal blends or coal blends with Soluble or Deposit addition was heated from ambient temperature to 300 °C at a heating rate of 10 °C/min and then to 1050 °C at a rate of 3 °C/min under a nitrogen atmosphere. After the temperature was maintained at 1050 °C for 30 min, the crucible was cooled down to room temperature to obtain the crucible coke.

The coke reactivity towards CO$_2$ was determined according to the reported method (Swietlik et al., 1999). Simply, 20 g of crucible coke (size in the range of 3–6 mm) was treated in a CO$_2$ flow of 500 L/min for 2 h at 1050 °C. The weight loss percentage of the coke after the treatment was defined as coke reactivity index (CRI). The micro-strength of coke was assessed in accordance with the Ragan and Marsh test (Ragan and Marsh, 1981). Briefly, two charges of cokes of 2 g (0.6–1.25 mm in particle size) were loaded into two separate cylinders (305 mm long and 25.4 mm i.d.), and each cylinders contained 12 steel balls (8 mm diameter). Then, the cokes along with the cylinders were rotated for 800 revolutions at a rotation speed of 25 rpm. The weight percent of coke particles with particle size of larger than 0.2 mm was defined as the micro-strength index (MSI) of the coke. The micro-strength of coke after CRI measurements was designated as coke strength after reaction (CSR) (Shui et al., 2013). The CRI and CSR were all carried out in duplicated runs with the errors less than 2%.

3. Results and discussion

3.1. Yield distributions of products

Fig. 1 displays the yield distributions of products obtained from degradative solvent extraction of RS and SD. It can be observed that the extraction temperature exhibit a great influence on the yield distributions. The yield of Soluble increased significantly with the temperature rising for both RS and SD, while those of Deposit reached a maximum at 300 °C. The sum of yields of extracts, Soluble and Deposit, was rather high at elevated temperature (300, 350 °C), especially reaching as much as 56.8% for SD at 350 °C. Biomass only decomposes slightly at around 250 °C due to the mild decomposition of hemicellulose (Sanchez-Silva et al., 2012), which should be the reason for the low extract yield at 250 °C. However, both the hemicellulose and cellulose decompose intensively at 280–350 °C (Pasangulapati et al., 2012), so the yields of the extracts increased obviously at the temperature of 300 and 350 °C. From the viewpoint of the extracts yields, the degradative solvent extraction of biomass should be conducted at the temperature higher than 250 °C.

3.2. Ultimate and proximate analyses

The ultimate and proximate analyses of raw biomasses and the extracts obtained are shown in Table 1. Similar trends of chemical composition variation of the extracts versus extraction temperature were observed for both RS and SD. Compared to raw biomasses, Soluble and Deposit contained obviously much higher carbon content and lower oxygen content respectively. In addition, the carbon content and oxygen content of Soluble increased and decreased with the extraction temperature rising, respectively. It was also the case for Deposit. This suggests that elevating extraction temperature can promote the deoxygenation of raw biomasses. Furthermore, the ash contents of the Soluble and Deposit were extremely lower than those of their corresponding raw material. This could be extraordinarily favorable for the subsequent utilization of Soluble and Deposit by mitigating the ash-related problems. To investigate the elemental composition variations, the atomic ratios of H/C versus O/C diagram of raw biomasses,
Solubles and Deposits are displayed in Fig. 2 (Van Krevelen diagram (Erdogan et al., 2015)). The abbreviation “RS-250-S” denotes Soluble produced from RS at 250 °C, and by this analogy. It can be observed that RS and SD fell within the typical biomass region. But Solubles and Deposit experienced a significant carbonization process with reduced H/C and O/C ratios, which were caused by dehydration and decarboxylation reactions (Parshetti et al., 2013). Fig. 2 shows that the Solubles and Deposits were more coal-like products from the viewpoint of the elemental composition. The carbonization severities of Solubles and Deposits increased with the temperature rising. But the Solubles and Deposits still contained relatively higher H/C ratios than that of coals. According to the hydrogen donor theory (Clemens and Matheson, 1995), richer hydrogen species may produce more mobile hydrogen donor to stabilize radical fragments formed from thermal cracking of coal macrostructure. It may be beneficial during cokemaking process after Solubles and Deposits addition.

3.3. Chemical structure analysis

The chemical structures of raw biomasses, Solubles and Deposits were investigated by FTIR technique, as shown in Fig. S1. The broad adsorption band in the range of 3200–3600 cm⁻¹ and 1000–1100 cm⁻¹ were respectively attributed to hydrogen bonding (–OH groups) and C–O groups, which were characteristic structure of cellulose (Eberhardt et al., 2010; Tandy et al., 2010). This indicates the raw biomasses were rich of oxygen-containing functional groups. However, Fig. S1 shows that the Soluble and Deposit have completely different structures compared to the raw biomasses. The peaks associated with oxygen-containing groups (such as –OH stretching and C–O stretching) dramatically weakened. Also, the intensities of oxygen groups (especially for –OH) in Soluble and Deposit decreased with extraction temperature increasing, which is consistent with the ultimate analysis, as shown in Table 1. The oxygen groups, including hydroxyl, are deleterious for coke-making since they can deplete the donor hydrogen and leading to the formation of cross-linked chars (Clemens and Matheson, 1995). Hence, the lower content of oxygen groups in Soluble and Deposit is beneficial for its use in coal blends. The peaks attributed to aromatic groups, such as aromatic C–H stretching vibration at 3050 cm⁻¹, aromatic C=C stretching band at 1460–1600 cm⁻¹ and aromatic out-of-plane C–H stretching at 750–875 cm⁻¹, were found to prevail in the spectra of both Soluble and Deposit.

3.4. Thermal decomposition behavior analyses

Fig. 3 presents TG-DTG curves of Solubles and Deposits obtained at 250–350 °C as well as the raw biomasses. The sharp peak between 280 °C and 400 °C observed in the DTG curves of both RS and SD were mainly attributed to the decomposition of hemi-cellulose and cellulose. All the Solubles and Deposits exhibited quite different decomposition behaviors compared to those of raw RS and SD. In general, Soluble and Deposit displayed lower weight loss rates over a wider temperature range. The weight loss rates of the Solubles decreased slightly with the extraction temperature increasing, which may imply that the Soluble obtained at lower extraction temperature contained more light components. As for Deposits, a greater difference appeared up among TG and DTG curves of them. Overall speaking, the weight loss of Deposits reduced with the temperature rising. There are two overlapped peaks in the DTG curves of Deposits from both RS and SD. The weight loss rates also weakened with the extraction temperature increasing, like Solubles. The temperature ranges corresponding to the weight loss of Deposits became wider with the extraction temperature increasing for RS, while those became narrower for SD. The difference should be caused by the different chemical structures of Deposits obtained from RS and from SD as shown in Fig. S1.

3.5. Softening and melting behavior analyses

The softening and melting behaviors of Solubles and Deposits were estimated by thermomechanical analysis (TMA). Fig. 4 shows the TMA profiles of Soluble and Deposit obtained from RS and SD. The TMA profile, displaying the normalized displacement of the sample, reaches −1.0 when the sample melts completely. As pointed out in previous study, raw biomass did not exhibit any melting or softening behaviors (Wannapeera et al., 2012). However, it is interestingly found that the displacements temperature range of all Solubles from both RS and SD were as low as 80–120 °C, which was much lower than the temperature points where the Solubles started to decompose, as shown in Fig. 3. Generally, the melting points of Solubles produced at elevated temperature shifted to higher temperature, although they all fell in a narrow temperature range of 80–120 °C. In comparison with the Solubles, there were obvious bigger differences among the softening or melting behaviors of the Deposits from either different extraction temperatures or different raw biomasses. The Deposits obtained at 250 °C from both RS and SD could completely melt at around 140 °C. The melting temperature of Deposit from SD at 350 °C shifted to higher temperature (180 °C), while the Deposit from RS at 350 °C did not show complete plastic behaviors. The different softening and melting behaviors of Soluble and Deposit are expected to have different effects on the thermoplastic properties of coal blends.

3.6. Thermoplastic properties of coal blends

The quality of produced coke greatly depends on the thermoplastic properties of the raw coals (Fernández et al., 2009). So the influence of the extracts addition on thermoplastic properties of coal blends was probed by Gieseler test. Table 2 shows the thermoplastic parameters of the GC and its blends with 2 wt% Soluble or Deposit additions. The plastic range of raw GC was only 74 °C. For Solubles addition, the softening temperature of coal blends decreased slightly, while the resolidification temperature of blends increased significantly. These leads to the enhancement of plastic range as high as 9 °C, especially for Soluble prepared at elevated temperature. The more significant enhancement of the plastic range of the blends with Solubles prepared at elevated
temperature should be attributed to the lower oxygen content and higher melting temperature in Solubles at higher temperature (Shui et al., 2015), as shown in Table 1 and Fig. 4. The Deposits obtained from both raw biomasses also increased the resolidification temperature and enhanced the plastic range of the blends, like Solubles. However, the additions of the Deposits obtained from RS increased the softening temperature of the blends slightly, especially for the Deposits produced from RS at 350 °C. This should be because that the Deposits produced from RS at elevated temperature cannot melt completely before resolidification as shown in Fig. 4. Additionally, it has been proved by the MOF model that the log (MF) value ranged from 2 to 3 was the optimum window to obtain a strong coke (Diez and Alvarez, 2013; Fernández et al., 2015). The log (MF) values of the GC with Solubles or Deposits addition nearly all fell within the optimum window. Thus, the thermoplastic properties of the coal were improved by incorporation of the Soluble or Deposit obtained from biomasses. So, it is expected that the coal blends with Solubles and Deposits addition can produce coke with good strength.

3.7. Coke quality evaluation

Coke reactivity index (CRI) and coke strength after reaction (CSR) are the two most important parameters to assess the coke quality and its behavior in the blast furnace (Shui et al., 2015). In general, the high-quality coke is supposed to possess a lower CRI and a higher CSR. In this work, the coke quality was evaluated by crucible coking process. It was found that the GC with RS-350-S or SD-350-D addition had widest plastic range of 83 °C and suitable values of log (MF), as shown in Table 2. So, the CRI and CSR of the raw coal blends and the blends with 2% additions of RS-350-S or SD-350-D were estimated. The results are

![Fig. 3. TG-DTG curves of raw biomass and Soluble, Deposit obtained from RS and SD at 250–350 °C.](image-url)
Thermoplastic parameters of raw GC and it with 2 wt% Soluble or Deposit additions.

The Soluble and Deposit obtained from biomasses could enhance the coke quality. Hence, it can be concluded that the additions of Soluble or Deposit into the coke-making coal significantly improved its thermoplastic properties. Furthermore, the addition of Deposit or Soluble markedly enhanced the coke quality through increasing coke CSR and reducing CRI. Therefore, the Soluble and Deposit prepared from degradative solvent extraction of biomass wastes were proved to be good additives for coke-making.

4. Conclusion

Soluble and Deposit with good thermoplastic properties were produced by degradative solvent extraction of biomass wastes under mild condition. The Soluble and Deposit had significantly higher carbon content, lower oxygen groups (such as –OH groups) and extremely lower ash content, compared to raw biomasses. The additions of Soluble or Deposit into the coke-making coal significantly improved its thermoplastic properties. Furthermore, the addition of Deposit or Soluble markedly enhanced the coke quality through increasing coke CSR and reducing CRI. Therefore, the Soluble and Deposit prepared from degradative solvent extraction of biomass wastes were proved to be good additives for coke-making.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2016.01.105.

References


Li, X., Ashida, R., Miura, K., 2012. Preparation of high-grade carbonaceous materials having similar chemical and physical properties from various low-rank coals by degradative solvent extraction. Energy Fuels 26, 6897–6904.


Wannapeera, J., Li, X., Worasuwannarak, N., Ashida, R., Miura, K., 2012. Production of high-grade carbonaceous materials and fuel having similar chemical and physical properties from various types of biomass by degradative solvent extraction. Energy Fuels 26, 4521–4531.
