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Rheological behavior of coal bio-oil slurries

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ABSTRACT

Coal bio-oil slurries (CBSs) were prepared by blending coal with bio-oil from the fast pyrolysis, and their apparent viscosities were measured by a rotary viscometer. The influences of coal rank, solid concentration, particle size distribution and temperature on the apparent viscosity and rheological properties of slurries were investigated. Additionally, the grey relational analysis was employed to determine the order of importance of factors affecting the apparent viscosity for different rank coals. Results show that, the CBS exhibits non-Newtonian fluid behavior and can be described by Herschel–Bulkley equation. The main factors for different rank coals affecting apparent viscosity of CBS are inherent moisture and carboxyl groups. The maximum solid concentration of CBS can reach 45–47 wt. % for Shenmu bituminous coal. Appropriate solid particle size distribution and preparation temperature can provide satisfied slurries with low viscosity.

1. Introduction

Biomass is an important alternative renewable and carbon neutral energy resource compared to the fossil fuels [1–4]. However, direct application of biomass is restricted due to its higher transport cost and lower energy density [5]. So it is favorable to convert biomass into bio-oil by pyrolysis, and the energy density can be increased significantly. Bio-oil exhibits high oxygen content [6–8], high water content [7], strong acidity and instability [9], and all this makes it difficult for direct application. Thus, bio-oil needs to be upgraded for further utilization.

One of the effective applications of bio-oil is to make slurries with char or coal. The properties of bio-char based slurries have been studied by many researchers [10–12], and the suspensions could be used in combustion and gasification. As a replacement of coal water slurry (CWS), Wang [13] proposed the feasibility of making coal bio-oil slurry (CBS) using biomass fast pyrolysis oil and preliminarily tested its gasification performance. With coal added into bio-oil, the suspensions have much higher calorific value than bio-oil, and the bio-oil in turn contributes much more heat to CBS than CWS with the same coal concentration. Thus CBS could also be used in combustion process and syngas production by gasification. Moreover the bio-oil derived from biomass in CBS does not increase CO_2 emission. Therefore, it could be considered as a partial green fuel.

In combustion and gasification process the slurry needs to keep high coal concentration for high calorific heat or syngas yield. It requires optimal solid loadings with low apparent viscosity simultaneously. Therefore, rheological behavior is an important parameter for pumping and atomizing of CBS slurry. The purpose of the present work is to investigate the effect of coal ranks (from lignite to anthracite), coal concentration and particle size distribution on the apparent viscosity and viscosity–temperature properties of CBS.

2. Experimental section

2.1. Materials

Bio-oil sample used in the study was from Shandong Yineng Bioenergy Co., Ltd, China. It was produced in a fluidized bed by pyrolysing rice husk at around 500 °C and its properties were summarized in Table 1. Elemental composition of bio-oil was measured by an elemental analyzer instrument (vario EL cube). The water content and pH value of bio-oil were determined by Metrohm Karl Fischer Titrino and a pH meter, respectively. The higher heating value (HHV) of bio-oil was determined by a calorimeter (XRY-1B, Shanghai Changji Instrument), and the lower heating value (LHV) of bio-oil was calculated by Eq. (1) [14,15].

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Nomenclature

CBS	coal bio-oil slurry
CWS	coal water slurry

$$\mathrm{LHV[J/g]} = \mathrm{HHV[J/g]} - 218.13 \times H\%[\mathrm{wt\%}] \tag{1}$$

Ten coal samples used in this work are from different areas, and their ranks are from lignite to anthracite. The proximate analysis and ultimate analysis of these coals are given in Table 2. Coals are ball milled to give the similar particle size distributions as shown in Fig. 1.

When investigating the influence of particle size distribution, coal from Shenmu (SM) was crushed and then ball milled for different time to obtain samples with different particle size distributions noted as S-PSD1, S-PSD2, S-PSD3 in Fig. 2(a). Samples with different proportions of S-PSD3 mixed with S-PSD1 are shown in Fig. 2(b). Coal samples were then dried at 105 °C for 4 h. Both higher heating value (HHV) and lower heating value (LHV) of SM coal (dry basis) were analyzed by a calorimeter (XRY-1B, Shanghai Changji Instrument). The HHV and LHV of SM coal are 22,724 and 21,815 J/g respectively.

2.2. Experiment and methods

Coal bio-oil slurries with different solid concentrations were prepared by adding coal particles into 100 g of bio-oil, and then they were stirred with a high speed agitator for 30 min until a homogeneous slurry formed. No emulsions were added in CBS.

Total acidic functional groups and carboxyl groups of coal samples were determined by $Ba(OH)_2$ and $Ca(CH_3COO)_2$, respectively, and the content of phenolic hydroxyl groups were calculated by subtraction [16,17].

The low-temperature nitrogen adsorption analysis was carried out in Quantachrome automatic physical and chemical adsorption instrument (AUTOSORB-1-C-TCD). All samples were measured at 77 K using nitrogen as adsorbate to obtain BET surface area and total pore volume.

The apparent viscosity of coal bio-oil slurries was measured by a rotary viscometer (NXS-11B, Chengdu Instrument Factory, China). A water bath was used to keep constant temperature of slurry samples. The details of apparent viscosity of CBS measurement were corresponded with the method of coal water slurry [18]. The experimental error of apparent viscosity was estimated based on the law of error propagation, which involves how random errors in the experimental measurements are propagated into errors in the quantity calculated according to the measurements [19]. The apparent viscosity was a function of shear stress as defined in Eq. (2), and the shear stress can be calculated from Eq. (3).

Table 1
The physical properties and elemental composition of bio-oil sample.

Physical properties	
Water content (wt.%)	43.77
pH	2.71
Viscosity at 25 °C (mPa·s)	9.23
HHV[a] (J/g)	12,481
LHV[b] (J/g)	10,692
Elemental composition (wt%)	
C	30.16
H	8.20
O^{diff}	60.64
N	0.96
S	0.04

[a] HHV, higher heating value.
[b] LHV, lower heating value.

Table 2
Proximate and ultimate analysis of coal samples.

Coal sample	$M_{inh,ar}$[a]	Proximate analysis (wt%)			Ultimate analysis (wt%)				
		V_d[b]	A_d[c]	FC_d[d]	C_d	H_d	N_d	O_d[e]	S_d
GC	3.94	31.95	8.64	59.41	74.98	4.10	1.05	10.87	0.35
YL	4.13	28.79	47.06	24.15	36.45	3.31	0.93	11.90	0.35
XL	9.87	31.79	26.39	41.82	54.96	3.86	0.82	12.99	0.98
FG	4.89	36.11	4.49	59.40	76.43	4.30	1.08	13.58	0.12
TX	0.85	11.19	5.29	83.52	87.01	3.20	0.70	3.55	0.26
BR	8.48	44.00	11.96	44.04	62.60	4.28	0.84	20.05	0.26
HN	1.57	10.36	24.14	65.50	67.03	2.37	0.61	3.69	2.16
TY	1.78	25.49	31.05	43.46	53.12	3.13	0.94	11.30	0.47
TS	1.22	23.58	30.40	46.02	57.76	3.20	0.94	6.81	0.88
SM	4.29	28.35	25.29	46.36	59.88	3.59	0.71	10.12	0.40

[a] Inherent moisture content in as received basis.
[b] Volatile content in dry basis.
[c] Ash content in dry basis.
[d] Fixed carbon content in dry basis.
[e] Oxygen content is calculated by difference. We assume that it does not include oxygen contained in ash.

$$\eta = \frac{\tau}{\gamma} \times 1000 \tag{2}$$

where η is apparent viscosity, mPa s; τ is shear stress, Pa; γ is shear rate, s^{-1}.

$$\tau = Z \times \alpha \tag{3}$$

where Z is a constant coefficient (0.5675) which does not change with shear rate, Pa; α is the reading in dial of the viscometer.

At certain shear rate, the apparent viscosity (η) is only determined by α. Thus the limit of error of η can be calculated based on equation (4).

$$\sigma_\eta^2 = \frac{Z}{\gamma}\delta_\alpha^2 \tag{4}$$

where σ_η^2 and δ_α^2 are the limits of error of η and α respectively, and δ_α is 0.1 for the viscometer. σ_η^2 at different shear rates are listed in Table 3. As shown in Table 3, the limits of error of apparent viscosity at all shear rates are in the range of 0.1538–1.7857, which is rather

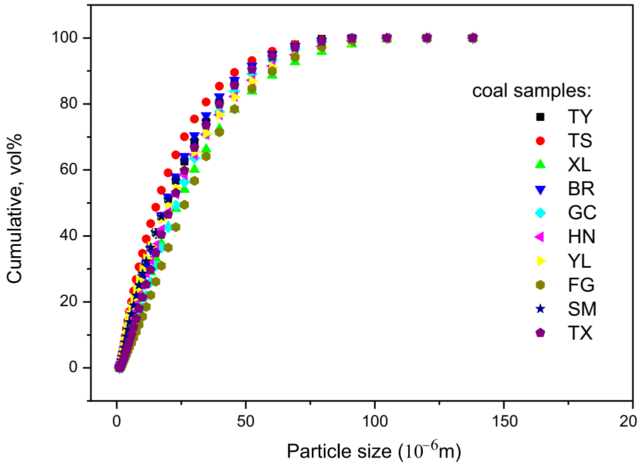

Fig. 1. Particle size distributions (PSD) of ten coal samples.