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Flow and yield stress behaviour of ultrafine Mallee biochar slurry fuels: The effect of particle size distribution and additives

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HIGHLIGHTS

- ▶ Polybutadiene-maleate is more effective in increasing the solids loading of biochar slurries.
- ▶ Unltrafine biochar slurries in excess of 40 wt% solids have been prepared.
- ▶ Yield stress decreases with increasing particle size of the biochar slurries.
- ▶ Power law models described the relationship between yield stress and particle size.
- ▶ The yield stress–volume fraction relationship of self-similar PSD slurries is also power law.

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ABSTRACT

The yield stress and flow behaviour of ultrafine Mallee biochar–water slurries were evaluated as a function of particle size distribution, solid concentration and additives including carboxymethylcellulose sodium salt (CMC) and poly(budadiene-maleic acid) sodium salt (BMA). The Mallee biochar was made from Oil Mallee chips carbonised in the absence of air at 750 °C in an indirectly-fired kiln with a solid residence time of ca. 30 min. The biochar–water slurries were prepared, with and without additives, by (1) dry-milling the biochar for different times and then mixing the resulting powders with water and (2) by wet-milling the biochar also for different times. The milling, dry or wet over different times resulted in different particle size distributions, the effect which on the rheological properties on the slurries was also investigated. The slurries displayed highly shear-thinning flow behaviour, typical of a flocculated dispersion. It was found that the yield stress decreased with increasing particle size and the relationship can be represented by a power law model. The yield stress showed a dependence on D_{50} (median diameter) or $D_{4,3}$ (volume average diameter) to the power of -0.8. In the presence of 1 and 5 dwb% BMA, the dependence on $D_{4,3}$ was to the power of -2 and -3, respectively. A power law model was also shown to describe the relationship between the yield stress and the solid volume fraction. The power law index ranged from 11.3 to 12.3 for slurries prepared from wet-milled biochar powders and from 14 to 18 for slurries prepared from dry-milled biochar powders. The highly charged BMA additive did not completely disperse the Mallee biochar slurries however it did reduce the yield stress and viscosity of the slurries significantly. Zeta potential data also strongly indicate the occurrence of BMA and CMC adsorption on the char particles. However, the CMC additive did not produce the significant reduction in the yield stress as expected.

1. Introduction

The preparation of ultrafine, concentrated coal slurry fuels of relatively low viscosity and with a suitable flow behaviour has gained increasing attention over recent times [1,2]. The aim is to produce a slurry fuel as a suitable replacement for diesel fuel for combustion in a compression ignition (CI) engine (diesel engine). The ultrafine nature of such a slurry fuel may also make it a suitable fuel for gas turbine combustion. The desired top-size for slurry fuels in these applications is as low as 20 μm for CI engines and 10 μm for gas turbine engines [3]. The likely median size should be 5–15 μm and 4–6 μm for the CI engines and gas turbines, respectively. Previous combustion tests of coal–water slurry (CWS) fuels in CI engines have typically employed quite coarse size distributions, with the largest size as high as 85 μm [4,5]. The coal–water slurry specifications used in the engine tests by GE and the Cooper and Arthur D. Little team are listed in Table 1 [4,5]. Note

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Table 1
CWS specifications for low speed CI engines [4,5].

Coal	Bituminous/sub-bituminous
Volatile content (daf basis)	27–41%
Mean coal size	5–12 μm
Top particle size	15–85 μm
Ash content (dry coal basis)	1–2 wt%
Sulphur (dry coal basis)	1–2 wt%
Solid content	48–55 wt%
Viscosity	<30 cP@50–1 s < 300 cP@1000–1 s
Additive	Dispersant (unknown)

that in the absence of commercial markets for CWS as an engine fuel, such specifications should be regarded as guidelines only.

It is well-known that particle size distribution (PSD) is a very important parameter in determining the rheological behaviour and solid loading of coal or char suspensions [6–17]. PSD affects the packing density of particles in suspension. A broad PSD, or the mixing of coarse and fine size particles in correct size fractions can and have been shown to greatly improve the particle packing density [18,19] and the solid loading of the suspensions, whilst maintaining a relatively low viscosity and yield stress [10,11,13]. This usually involves mixing fine particles with a median diameter of tens of microns with coarse particles of several 100 μm in diameters. Only recently did the study of ultrafine coal slurries dispersed in oil or water has gained significant interests [1,2]. Cui et al. [1] evaluated the rheological behaviour of ultrafine coal–oil slurries with median diameter of 2.71 μm at concentrations ranging from 45 to 55 wt% coal (sub-bituminous). The slurries were found to display a slight shear-thinning behaviour only. Cheng et al. [2] also reported shear-thinning behaviour for their ultrafine coal–water slurries. This shear-thinning behaviour is normally associated with the net colloidal force interacting between particles being attractive. This is true provided that the suspending medium is a Newtonian fluid [20,21]. Low viscosity oils are generally Newtonian. In general, as the colloidal content is increased and the colloidal force being net attractive, the slurry will become more non-Newtonian i.e., more shear-thinning in behaviour [20,21]. The motivation for this investigation is that there is currently no rheological study being conducted on ultrafine biochar slurries.

For ultrafine suspensions, surface or interparticle forces will play a critical role in governing their behaviour. These forces, in turn, are controlled by the surface chemistry of the system such as pH, ionic strength and the nature of the adsorbed additives. Additives such as polyelectrolytes are often employed to increase or reduce the strength of attractive force between particles [21–24]. The effect of these forces on colloidal slurry rheology can be very significant; the changes to the viscosity can be several orders of magnitude and the yield stress can be made to disappear or increase by few orders of magnitude [21–24]. Additives that function as a dispersant or wetting agent are often added to reduce viscosity or increase the solids loading of the suspensions. In this study, additives will be used to control solids loading and slurry behaviour. Additives are often used in coal–water slurry preparation to reduce viscosity or impart shear-thinning characteristics and stability [12,14,15,17,25–31]. A polymer or macromolecules such as CMC [32], guar gum [33] xanthan gum or polysaccharides [34] is used to promote slurry stability.

2. Materials and experimental methods

The material used was an Oil Mallee biochar less than 1 cm in sizes as received. The Mallee biochar was made from Oil Mallee chips carbonised in the absence of air in a pilot-scale rotary kiln operating at 750 °C and with a solid retention time of approximately 30 min. The ultimate and proximate analysis of the biochar is given in Table 2. The high sulphur (0.22 wt%) and high ash (15.6 wt%) contents of this Mallee biochar may not be unusual as Oil Mallee trees can grow in a high salt environment [35]. The ash content is expected to be lower for trees grown in low salt regions.

The additives used were carboxymethyl cellulose sodium salts (CMC) of molecular weight (MW) 700,000 g/mol and poly(butadiene-maleic acid) (BMA) of MW 10,000–15,000 g/mol. These additives were sourced from PolyScience Inc, USA. Sodium hydroxide solution was added in stoichiometric proportions to fully charge the BMA polyelectrolyte.

A high-energy SPEX8000 mixer/mill was employed for dry and wet grinding of the biochar particles. In wet grinding, a fine slurry is produced as the product. In a typical milling, a powder charge of 10 g and as many as 10 harden steel balls of 9.5 mm in diameter (and as few as 2 balls) were loaded and sealed in a hardened steel vial with a volume capacity of 86 ml. The char samples were milled from 10 to 60 min, resulting in samples with a range of median particle sizes (D_{50}) and particle size distributions. In the case of wet milling, 1 dwb% of additives was added to the mixture.

For dry-milled biochar, the next step was to formulate a slurry with a specific solid concentration. The majority of biochar–water slurries contained in excess of 40 wt% of solids and 1 wt% of a dispersant [17]. The particle density was determined using a 10 ml density bottle, using a dilute slurry of known solids concentration. It was found to be ~1.50 g/ml.

To prepare a slurry, an appropriate amount of a dispersant was firstly dissolved in a given mass of water to form a surfactant solution of typically 4 wt%. Slurry samples with solid loadings ranging from 30 to 60 wt% were then prepared using these surfactant solutions, with the amount of surfactant roughly equalling to 1 wt% of the dry solid mass. Once the constituents were added, the slurry was mixed either by hand or, for particularly viscous samples, through the use of a digital sonicator. When thoroughly mixed, the slurry samples were then ready for rheological characterisation.

A laser sizing equipment, the Malvern Mastersizer Microplus, was employed to characterise the particle size distribution of the slurries. The yield stress of the slurries was measured with a range of Brookfield DV II + Pro vane viscometers, each with a different spring constant. A vane was immersed in the slurry and rotated at a very slow and constant speed of ~0.4 rpm. The maximum torque recorded was then used in the yield stress calculation. A Haake VT550 cone-and-plate viscometer was also employed to characterise the flow or shear stress-shear rate behaviour. The zeta potential of the biochar slurries was measured with a colloidal dynamics ZetaProbe.

3. Results and discussion

3.1. Wet milled slurries

The effect of grinding time on the (cumulative) particle size distribution (PSD) of wet ground 41 wt% Mallee biochar slurries is shown in Fig. 1. The particle size is rescaled with the median diameter, D_{50} in the plot. If the cumulative volume percent versus D/D_{50} data at all grinding times fell on the same master curve then the PSD is self-similar. The fineness of the grind can therefore be represented by one parameter, i.e. the median diameter [36]. With these self-similar PSDs it may also be possible to correlate the rheological properties of the suspensions such as yield stress and viscosity, with only one size parameter. The grinding time employed in this study ranged from 10 to 60 min. The plots in Fig. 1 showed that the PSD curves at all grinding times are quite self-similar with