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Research article

# Rheological behaviour and stability characteristics of biochar-water slurry fuels: Effect of biochar particle size and size distribution



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#### A R T I C L E I N F O

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#### ABSTRACT

The effect of particle size and size distribution on the rheological properties and stability characteristics of biochar-water slurry fuels was investigated. The biochar-water slurry fuels were prepared by dispersing biochar samples in water as the suspending medium. Slurries with varied median particle size ( $D_{50}$ ) of biochar, unimodal size distribution of biochar with varied  $D_{50}$ , and bimodal size distribution with varied size ratio of coarse to fine fractions ( $\lambda$ ) and varied fine particle fraction content ( $\xi$ ) were prepared. The yield stress of the slurries prepared was measured using a Brookfield vane viscometer while the dependence of the apparent viscosity and shear stress on the shear rate was characterised using a Haake VT550 cone and plate viscometer. The stability of the slurry fuels was characterised using a "drop rod" method. At a given biochar loading, the yield stress of the slurry fuel first decreased slightly with increasing  $D_{50}$  for  $D_{50} < -15 \,\mu$ m and then increased dramatically with further increasing  $D_{50}$  due to the stronger water uptake capacity of larger biochar. The biochar of bimodal size distribution reduced the viscosity and thus increased maximum biochar loading. The viscosity was further reduced as  $\lambda$  decreased, being more profound at smaller  $\xi$ . The slurry fuels prepared with finer biochar were more stable. The stability of slurry fuels of bimodal particle size distribution was greater at higher  $\xi$  for a given  $\lambda$ .

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#### 1. Introduction

Pyrolysis of biomass to produce a pyrolysis fuel gas mixture rich in hydrogen, methane and carbon monoxide, and a solid biochar residue has been proposed as a means of biomass energy utilisation in remote and distributed installations [1–5]. The pyrolysis gas can be directly burned in internal combustion gas engines for electric power generation [6] while the biochar can be made into slurry fuels that can be burned in low and medium speed diesel engines for combined heat and power generation [6,7]. This is suitable in remote or regional areas, where power is currently produced from diesel generators and where biomass is usually an abundant primary energy resource [6–9].

The primary challenge for the biochar-water slurries to be used in diesel engine is to achieve appropriate rheological properties suitable for storage, pumping and atomisation for efficient combustion while still maintain a suitably high solid loading. It is known that slurries with high solid loadings and desirable rheological properties can be achieved by changing the particle size and size distribution of the solid [10]. For instance, coal-water slurry fuels prepared using solids of broad particle size distributions possess lower viscosities than those with narrow particle size distributions [11–15] since the fine particles occupy the voids between the coarse particles, resulting in a reduction

\* Corresponding author. *E-mail address:* mingming.zhu@uwa.edu.au (M. Zhu). in viscosity and an increase in solid loading [10,16,17]. The particle size and size distribution also affect the stability of the resulting slurries. Coal-water slurry fuels prepared using larger particles tend to form hard sediment more quickly, as larger particles tend to settle out faster than smaller particles, resulting in less stable slurry fuels [18]. There is often a trade-off between viscosity and stability as solid particles tend to settle out more quickly in a slurry with lower viscosity [19].

It has been found that biochar, as a porous material, is able to uptake water into intra-particle internal pores, known as water uptake capacity [20]. For biochar with different particle sizes, the internal pores can vary and thus result in varied water uptake capacity [20]. Water used for the biochar-water slurry fuel preparation would first fill the intra-particle pores, resulting in less water acting as suspending medium and an increase in the particle number concentration (n) (defined as the biochar particle number per unit volume of the suspending medium) [21]. In addition, the apparent density of biochar increases as water enters their internal pores. The increase in both n of slurry fuels and in apparent density of biochar due to the water uptake capacity will in turn affect the rheological properties and stability characteristics of resulting slurry fuels [22].

Building on our previous work [8,9,14,16,23] and aiming to prepare stable biochar-water slurry fuels with high solid loading and the desired rheological properties, the present work specifically focused on the effect of biochar particle size and size distribution on the yield stress, viscosity and stability characteristics of biochar-water slurry fuels.



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Table 1
Proximate and ultimate analyses and calorific value of the biocha

Proximate analysis (wt% db)			Ultim	ate an	alysis	(wt% (	daf)	Calorific value (MJ kg <sup>-1</sup> , db)	
VM	FC	Ash	С	Н	Ν	S	0 <sup>a</sup>		
7.2	89.2	3.6	86.3	1.6	0.3	0.6	11.2	32.0	
<sup>a</sup> By	differer	nce.							

#### 2. Experimental

The as received biochar was produced by pyrolysing a pine sawdust in an indirectly fired kiln reactor operating at 750 °C in the absence of air, with a retention time of ca. 25 min [7]. The proximate and ultimate analyses of the resulted biochar samples are given in Table 1.

To obtain biochar samples with different particle sizes, the as received pine sawdust biochar was first ground to fine particles with size fraction less than 106 µm, which was then sieved to different size fractions: 0-10, 10-20, 20-32, 32-45, 45-53, 53-71, 71-90, and 90-106  $\mu$ m, with the median particle size ( $D_{50}$ ) being 5.2, 14.7, 21.0, 39.4, 48.2, 61.3, 70.1, and 85.1 µm, respectively. The particle size distribution of each sieved biochar size fraction, characterised by a CILAS 1180 particle size analyser, is shown in Fig. 1(a). The proximate and ultimate analyses of the sieved biochar samples are given in Table 2. It shows that there was no significant difference between different fractions of biochar in terms of chemical composition. The as received biochar was also ground for various milling times of 4 s to 1 h, to obtain biochar samples of varying size distributions, with the median particle size  $(D_{50})$ being 21.9, 17.6, 15.6, 13.9, 11.8, 8.2, 6.5, 4.8, 4.0, and 2.2 µm, respectively. The size distributions of the resulting biochar samples are shown in Fig. 1(b). It is evident that all the samples were of unimodal size distributions. Biochar samples of bimodal size distribution were then obtained by mixing a coarse one ( $D_{50} = 11.8, 13.9, 15.6, 17.6, \text{ and } 21.9 \,\mu\text{m}$ , respectively) and a fine one  $(D_{50} = 2.2 \,\mu\text{m})$ , with the fine fraction ( $\xi$ ) in the mixtures varying from 0 to 100 wt%. The resulting size ratios of the coarse to fine fractions ( $\lambda$ ) were 5.3, 6.3, 7.0, 7.9, and 9.9, respectively. All biochar samples thus prepared were dried in an oven at 110 °C for 24 h to remove moisture prior to biochar-water slurry fuels preparation.

The water uptake capacity of biochar was measured using a method [20] as follows. A dried biochar sample was first weighed and dispersed in water and held for 24 h to ensure that the biochar was soaked with water. The biochar/water mixture was then transferred to a weighed 30 ml centrifuge tube and centrifuged for 15 min at 3500 rpm. The centrifuge tube was then placed upside down to allow a free drainage of excess water for 10 min. As a small amount of fine biochar particles would inevitably flow out with the water drained from the tube, the weight of the remaining biochar was determined by the biochar sample again at 110 °C for 24 h. It was revealed that the amount of biochar lost in with the drained water was less than 1 wt%, as such, this small discrepancy

#### Table 2

Proximate and ultimate analyses and BET surface areas of biochar samples with various particle sizes.

Particle size (µm)	Proximate analysis (wt% db)			Ultim (wt%	ate ai daf)	nalysi	BET surface area $(m^2 g^{-1})$		
	VM	Ash	FC	С	Н	Ν	S	0 <sup>a</sup>	
0-10	6.8	4.0	89.2	86.4	1.5	0.3	0.5	11.3	317.3
10-20	6.9	3.7	89.4	86.4	1.4	0.3	0.6	11.3	282.5
20-32	6.7	3.7	89.6	85.5	1.4	0.3	0.6	12.2	251.0
32-45	7.4	4.0	88.6	86.1	1.4	0.3	0.6	11.6	220.5
45-53	6.9	4.5	88.6	85.2	1.4	0.4	0.5	12.5	209.7
53-71	7.6	3.9	87.5	86.1	1.6	0.3	0.6	11.4	189.7
71-90	7.1	4.3	88.6	85.6	2.0	0.3	0.5	11.6	158.2
90-106	7.2	4.4	88.4	86.5	1.8	0.3	0.6	10.8	142.4

<sup>a</sup> By difference.

was subsequently ignored in the determination of water uptake capacity. The water uptake capacity ( $\eta$ ) of biochar was then calculated according to Eq. (1) below [20]:

$$\eta = \frac{m_{cr} - m_c - m_b}{m_b} \tag{1}$$

where  $m_{cr}$  was the weight of centrifuge tube with remaining biochar and water,  $m_c$  the weight of centrifuge tube,  $m_b$  the weight of biochar used.

Slurry fuels were prepared by directly mixing biochar with deionised water without using any additives. Briefly, a biochar sample was taken, weighed and then added to a known amount of deionised water so that the biochar loading was varied between 25 wt% and 55 wt%. To ensure the uniformity of slurry fuels, each slurry fuel sample was thoroughly mixed using a digital sonicator with a 1 in. probe prior to the rheological measurement and stability characterisation.

The yield stress of a slurry fuel sample was measured using a Brookfield vane viscometer. A 4-blade vane was placed into the slurry fuel and rotated at a constant speed of 0.8 rpm. The maximum torque recorded was then used to calculate the yield stress [14,23,24]. A Haake VT550 cone-and-plate viscometer was used to quantify the dependence of apparent viscosity and shear stress on shear rate. For slurry fuels, the viscosity increases as solid loading is increased, making them more difficult to pump and atomise at high solid loadings. In practice, the maximum particle loading is often defined as the loading at which the viscosity of the slurry reaches 1000 mPa ·s at a shear rate of 100 s<sup>-1</sup> [25,26]. The calorific value of a slurry fuel was calculated based on the calorific value of the biochar and the biochar loading in the slurry fuel [8,9].

A less stable slurry fuel would incur the formation of a hard sediment at the bottom of the vial over time during storage. A slurry fuel with



Fig. 1. Particle size distributions of (a) sieved biochar samples, and (b) biochar samples obtained from different milling times.

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