Preparation and Rheology of Alcohol-Water Char and BioChar Slurry Fuel.

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ABSTRACT

Ethanol and methanol were added to increase the volatile content of the aqueous low ash and low sulphur, lignite and mallee char slurry fuel. Lignite char slurries were prepared in aqueous solutions of ethanol with content ranging from 5 to 50wt% ethanol. The yield stress of the slurry was measured as function of solids concentration. A carboxylate acid dispersant was found to be effective in dispersing char particles in alcohol-water mixtures, especially those slurries with low alcohol content. This is indicated by the maximum solids loading achieved decreasing with alcohol content in the solution. This maximum loading is ~ 65wt% for 100% water and reduced to ~57wt% for 50:50% water-ethanol mixture. This trend was unchanged when the density difference between the solutions was taken into consideration by using volume fraction of solids as concentration in the plot. Without the dispersant, the maximum loading obtained is much lower. Viscometry results showed dilatant flow behaviour for the highest loaded slurry and Newtonian behaviour for dilute slurries. Lignite char slurries with of a top size of less than 32 micron were also prepared at concentration up to 60 wt% solids in 40wt% ethanol and methanol solution with the aid of 1wt% D102 dispersant. These slurries are close to meeting the specifications required as a diesel fuel replacement. A relatively low solids loading of less than 50wt% was obtained with fine Mallee char slurry prepared in 40wt% alcohol solution.

Keyword: Biochar, Slurry Fuel, Coal, Yield stress, Viscosity, Ethanol, Methanol

INTRODUCTION

As the demand for energy increases around the world, current fuel sources become more expensive and alternative technologies previously deemed unviable are now becoming potentially suitable alternatives. These alternatives can ease the burden on producing ever larger quantities of predominantly fossil fuels whilst increasing the ease of supply and minimizing the environmental footprint. One such fuel that can be investigated as an
alternative to diesel fuels is slurry fuels. A slurry fuel can be widely described as a liquid medium containing a quantity of suspended combustible solids. These solids are usually finely ground to increase the surface area for combustion and reduce the degree of settling that will occur. Additives may be used to slow the settling process and increase the concentration of solids that may be suspended in the medium. Slurry fuels are a relatively old concept, with Smith and Munsell (1879) filing the patents for liquid slurry fuel in 1879. The fuel they developed was capable of being spray injected and piped, which was unique for fluids with suspended particles at the time. Following their initial development, slurry fuels have been used with a variety of components to help improve the energy density and reduce the costs involved (Papachristodoulou & Trass, 1987). In the past, coal has been the most common source of combustible solid used, primarily due to its’ availability, though biomass solids, such as charcoal, have been employed in the past too (N'kpomin et al., 1995). The major restraint to the development of slurry fuels have been the comparative costs involved with creating the specialized equipment and retrofitting combustors previously used with hydrocarbon fuels, as well as the expense of the slurry fuel itself. Hydrocarbon fuel sources have the ability to take advantages of scale, making components and supply cheaper. However, crude oil prices have consistently increased in the last 20 years, with the price rising from $US45 per barrel in 1990 (Delucchi et al., 1994) to $US120 per barrel in April 2011, far higher than the $US64 per barrel predicted by the US Energy Information Administration in 1990 (Delucchi et al., 1994). In light of these faster than anticipated increases in price, slurry technologies have become increasingly relevant as possible supplements, or even replacements in areas that have higher than average crude oil costs, due to factors such as supply problems or demand requirements.

A slurry fuel is usually composed of three classes of components. There is a liquid medium, a combustible solid in particle form and a range of additives to improve stability and modify the rheological properties. In most cases, the additives are kept to a minimum to reduce the cost of the fuel and reduce the likelihood of undesirable side effects including increased volatility and viscosity changes (Shukla et al., 2008).

Since the aim of slurry fuel is to maintain a high energy density, the combustible solid is usually maintained at a high concentration. Coal is most commonly used and concentrations of between 50% and 75% can be achieved depending on the medium and stabilizers used (Papachristodoulou & Trass, 1987). It is this concentration, along with the size distribution of the particles (Leong et al. 1993, Boylu et al., 2004, Chen et al. 2010), that has the greatest impact on the slurry’s rheological properties, as the interactions between coal particles and that between coal particles and liquid medium become far more complex that can potentially cause non-Newtonian fluid behaviour (Atesok et al., 2002). Past research has indicated that slurries tend towards Newtonian fluid behaviours at low shear rates, whilst increased shear rates can cause shear thinning (Papachristodoulou & Trass, 1987; Lin & Brodkey, 1985).
Charcoal is a more recent revelation within the slurry fuel industry, and is considered by many to be a more viable solid for use in these fuels due to its availability, economic credentials and renewable nature (May & Awang, 2009, Patton et al., 2010). Preliminary studies have found that the charcoal slurries contain a lower quantity of impurities (Patton et al., 2010) and are at least as volatile as a comparable coal slurry fuel (May & Awang, 2009). However, this area has not been as extensively investigated as coal slurries and issues such as maintaining the wood supply and lack of knowledge regarding rheology and volatility means that additional research and analysis is required to test the charcoal slurry’s usefulness as an alternative fuel source.

Coal and charcoal are both classed as carbonaceous solids and sourced from the same basic organic matter. Both solid types possess a range of impurities including base metals, sulphurs and other ash substances. Much of these impurities are not combusted along with the carbons, and as such will either remain as solids, generally referred to as ash within the combustion chamber, or be expelled as pollutants in the gaseous phase (Patton et al., 2010). As such, the substances present within coal and charcoal are similar, with the primary difference being the percentage of the composition of each of these impurities (N'kpomin et al., 1995). To use char or coal slurry as diesel fuel, the combustion engine must tolerate a higher concentration of ash minerals and sulphur (S) content. Engine grade coals or chars have average ash content of 0.8wt%, S content of 1wt% and nitrogen content of 2 wt% (Patton et al. 2010) as compared to 0.1wt% ash and 0.0015wt% sulphur content for diesel fuel. During operation these ash minerals are often deposited within the combustion chamber and are not expelled along with the gaseous burn off (N'kpomin et al., 1995).

Most slurry fuels are designed to be capable of spray injection and this helps define the required properties of the liquid medium that is to be used. One of the major associated issues with the use of aqueous char slurry fuel is the lack of volatile materials which were burnt-off during the charring process. Another issue with using water alone as the suspending medium is that water inhibits combustion, leading to wasted energy which can either dehydrate the fuel prior to combustion (Khiil'ko & Titov, 2008) or simply result in a less active fuel source (Miccio et al., 1997). As such, alcohols with a percentage of water is included to help maintain the desired rheological properties (Papachristodoulou & Trass, 1987) and good combustion behaviour. The use of alcohols must also be carefully monitored to avoid the slurry becoming too volatile (Shukla et al., 2008).

Additives, in particular dispersants and particle size distribution modification (eg. Leong et al. 1993, Boylu et al 2005, Chen et al. 2011) are the two most important parameters employed for increasing the solids loading of coal slurries. Additives play a number of roles and these include i) wetting and dispersing coal particles in water so as to achieve maximum coal loading (eg. Akta & Woodburn 2000, Atesok et al 2005, Chen et al 2011), ii) enhancing of slurry stability by preventing the formation of hard sediment cake (Boylu et al 2005) and iii) imparting shear thinning rheological behavior for high shear rate atomization (Natoli et al 1985). The relationship between the coal-type and the nature or
chemical structure of the additives to use is still unclear at present despite the numerous publications on coal slurry fuel additives (eg Akta & Woodburn 2000, Atesok et al 2005, Chen et al. 2011). This is further being complicated by the fact that surface oxidation and mineral ash content have a significant impact on the effectiveness of the additives used.

Current developments in slurry fuel technology have focused primarily on improving the cleanliness of the combustion and increasing the solid concentration in suspension. Methods of removing harmful products such as sulphur compounds and ash content are investigated as these processes both reduce the environmental impact and help improve the efficiency of the fuel (Liu et al., 2009). Other investigations focus on methods of improving the coal quality by blending coal sourced from different mines in order to enhance the favourable qualities of both (Gu et al., 2008).

MATERIALS AND METHODS

The materials used in this investigation were lignite char, mallee biochar, methanol, ethanol and water. Fine char slurry fuels of different compositions were prepared in ethanol-water and methanol water mixtures. The yield stress of the slurry was monitored as a function of solids concentration at various fixed composition of alcohol-water mixture. The ultimate and proximate analyses of these char are given in Table 1. The chars have a relatively low volatile matter content of less than 5% and a very low sulphur content making it a very clean fuel.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (wt%)</th>
<th>H</th>
<th>N</th>
<th>S (total)</th>
<th>O(by diff)</th>
<th>Ash</th>
<th>Volatile matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mallee Char</td>
<td>80.1</td>
<td>0.21</td>
<td>0.30</td>
<td>0.22</td>
<td>3.6</td>
<td>15.6</td>
<td>4.1</td>
</tr>
<tr>
<td>Lignite Char</td>
<td>92</td>
<td>0.38</td>
<td>0.67</td>
<td>0.21</td>
<td>2.8</td>
<td>3.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The fine char powders were produced by milling with a SPEX8000 high energy ball mill with 10 gram samples being grounded for 30 minutes. The particle size distribution (PSD) of the lignite char is shown in Fig.1. The \(d_{50}\) is \(6 \mu m\). The PSD is relatively narrow with a size range of 0.39 to 33 \(\mu m\).

Ethanol-water solutions with composition of 5%, 10%, 30% and 50wt% ethanol were first prepared. A 40wt% methanol solution was also prepared. In the slurry preparation, the mount of char to be used is predetermined. Then a 1 dwb% (g/100g char) D102 dispersant was first dissolved in an appropriate amount of the solution. The powder and the solution were then mixed and a fresh solution (with no D102) was added until wet slurry is formed. The mixture was then sonicated with a sonic probe. The yield stress was measured with
vane Brookfield viscometers with different spring constants. The flow behavior of some of these slurries was measured with a Haake VT550 cone-and-plate viscometer.

Fig. 1: The particle size distribution of the lignite char slurry.

RESULTS AND DISCUSSION

Dispersants are commonly used to reduce viscosity and to increase the solids loading of slurry to a level that can still be handled by the processing equipment. The effects of anionic dispersant D102 on the yield stress-solids concentration behaviour of slurries prepared in 10 and 50wt% ethanol solutions is shown in Fig. 2. Included in the plot for comparison are those prepared with no dispersant. It can be clearly seen that the dispersant

Fig. 2: The yield stress versus concentration behavior of aqueous-ethanol coal char slurry showing the effects of anionic dispersant D102.
is extremely effective in increasing the solids loading of the slurry, despite the presence of ethanol. The increase is very significant, from ~55wt% to ~65wt%, however D102 becomes less effective at a higher ethanol content. The mechanism responsible is known as charge-steric or electrosteric stabilization via the adsorbed D102.

Figure 3 shows the yield stress versus solids concentration behaviour of lignite char slurries prepared with ethanol solutions containing 10 to 50wt% ethanol. A slightly higher solids concentration was achieved with that prepared using the lowest ethanol content solution. The 30 and 50wt% ethanol solutions appeared to produce an identical yield stress-concentration character. The difference may become more apparent if plotted against volume fraction of solids as the density of the two ethanol solutions are quite different. The density is 0.952 g/ml and 0.918g/ml for the 30 and 50wt% ethanol solutions.

![Fig. 3: Yield Stress –solids concentration relationships of lignite char slurries prepared in ethanol solutions without dispersant.](image)

Figure 4(a) shows a similar plot for slurries prepared with 1wt% D102 additive. Figure 4(b) is the same plot but the solids concentration is expressed in vol% to take in account of the differences in density of the different ethanol solutions. The ethanol solutions used ranged from 5 to 50wt% ethanol. The density of 5, 10, 30 and 50 wt% ethanol solutions taking into account of non-ideal mixing is 0.99, 0.981, 0.952 and 0.918 g/ml respectively. D102 generally increases the solid loading of the slurries for any given ethanol solution. The most loaded suspension is the one prepared with least amount of ethanol in the solution. The trend remained the same even when vol% solids was used in place of wt% solids as shown in Fig. 4(b) except that the vol% value is smaller.

Figure 4(b) shows that the maximum volume percent achieved is much less than 60 for any given ethanol solution. The value is even smaller when 50wt% ethanol solution is used, < 50%. The maximum packing volume for random packing of a monodisperse sphere is
60.5%. The volume fraction obtained is therefore considered to be quite high although the particles in the slurry are not monodisperse.

Anionic D102 additive acts to disperse char particles in the ethanol-water mixture by providing electrosteric stabilization. It is adsorbed on the char particles and imparts charge and steric stabilization. At high ethanol content, this function was affected or inhibited. However, there are negatives associated with reducing the ethanol content of the slurry, as energy density and combustion efficiency will also be reduced (Shukla et al., 2008).

![Figure 4: Yield stress of lignite char slurries with 1% D102 additive as a function of a) wt% and b) vol% solids](image)

The slurries prepared by D102 additives tend to exhibit dilatant flow behavior, where the viscosity increases with shear rate at high solids loading [Chen et al. 2011]. Similarly, the slurries prepared with D102 additives and ethanol solutions appeared to display a small degree of dilatant flow behavior as shown in Fig. 5. The adsorbed additive imparts a strong repulsive force between the interacting particles. At high particle concentration, this repulsive force keeps the crowded particles at an equilibrium position. Any disturbance of this equilibrium such as in flow will encounter a strong repulsive force that needs the expansion of energy to allow the sliding of particles past one another in flow.

With regard to the development of char slurry fuel as a diesel fuel replacement, an important milestone has been achieved recently. For diesel engine application, the slurry fuel must have a top size of less than 30 micron. Very fine lignite char slurries of high solids loading have been prepared in 40wt% ethanol and methanol solutions. The PSD of these slurries are shown in Fig. 6. More than 99 wt% of the particles in both slurries were less than 30 micron. The PSD of the slurry prepared with 40wt% methanol is different to that prepared with 40wt% ethanol. The $d_{50}$ of the methanol solution slurry is less than 1 micron while in the ethanol solution is 2 micron. The reason for this difference is not clear despite the same master batch of char powder being used in the slurry preparation.
Fig. 5: The viscosity versus shear rate behavior of lignite char slurries prepared with different ethanol content.

Fig. 6: The particle size distribution of these fine lignite slurries prepared in 40wt% alcohol solution.

Figure 7 shows yield stress versus solids concentration plots of these lignite char slurries prepared with 1wt% D102. The zeta potential of 40% ethanol-water slurry is -10mV at pH 9 and conductivity of 0.35 mS/cm. For the 40% methanol slurry the zeta potential is -6mV.
at pH 8.8 and conductivity of 0.46 mS/cm. Despite the very fine size or high particle number concentration, a very high solids loading approaching 60wt% was achieved. The high number concentration increases the density of particle-particle interactions leading to higher amounts of energy being dissipated. However, the total energy being dissipated can be reduced by making the net particle-particle interactions repulsive. The onset of exponential growth in the yield stress was observed to occur at greater than 55wt% solids. The amount of hydrocarbon in these two fuels is about 76 wt% with the alcohol volatile accounting for 21% based on the total hydrocarbon content.

![Graph](image1.png)

**Fig. 7**: Yield stress versus concentration plots of fine lignite char slurry prepared in 40wt% alcohol solution.

![Graph](image2.png)

**Fig 8**: The effect of solids concentration on the yield stress behaviour of Mallee Char slurries prepared in 40wt% ethanol and methanol solution with 1dwb% D102.
Mallee char with particles passing a sieve size of 38 micron was used in the slurry preparation. The maximum solids loading obtained with the Mallee char slurries in 40wt% methanol and ethanol solutions is much lower than that obtained with lignite char. This trend was also observed previously with water as the suspending medium (Chen et al. 2010). Both ethanol and methanol solutions produced almost identical yield stress-concentration characteristics.

CONCLUSIONS

An anionic dispersant D102 was found to increase the solids loading of the lignite char suspension in ethanol-water suspending medium by as much as 20% at the maximum loading conditions. The electrosteric stabilization of the char particles by the adsorbed additive is therefore still effective in the presence of alcohol. Fine lignite char slurry with a top size of less than 32 microns approaching 60wt% solids has been prepared in both 40wt% ethanol and methanol solutions in the presence of 1wt% D102. Fine mallee char slurry prepared in 40wt% alcohol attained a much lower maximum loading less than 50wt% solids.

REFERENCES