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Development and rheological characterisation of an industrial liquid fuel consisting of charcoal dispersed in water

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Developing an industrial liquid fuel based on charcoal and water was the target of the present work. The relevance of this study is justified by the high energy potential of charcoal, its renewable nature, the easiness of storage and transportation in the liquid form, and by all the associated economic and environmental advantages derived thereof.
The ability of a commercially available charcoal to be dispersed in water was evaluated by analysing the rheological behaviour of the resulting charcoal water slurries (ChWS). The charcoal was ground in a conventional ball mill and dispersed in water with the aid of different surfactants. The effects of the most relevant factors influencing the rheological properties of the suspensions were evaluated, including: (i) type of surfactant and its added amount on the fuel viscosity (η) at a given solids fraction; (ii) the charcoal content, which should be as high as possible. The results enabled selecting the most efficient surfactant and its optimal amount required for minimising the fuel viscosity (η) and enhancing the stability of the suspensions. Stable ChWS containing 60 wt.% solids and 1 wt.% surfactant and exhibiting adequate flow properties were successfully obtained.

1. Introduction

The search for new energy sources is endless, being one of the most important concerns nowadays. The petroleum crisis, accompanied by an overall increase in oil prices and its limited abundance, led to the search for new ways of using coal as an energy source. However, handling, transportation and storage of solid coal is difficult and not safe due to the risks of spontaneous combustion. These drawbacks stimulated investigations aiming at using coal in liquid state [1–5].

Liquid fuels can be produced via either direct or indirect coal liquefaction methods [1], or by preparing coal water slurries (CWS) [1–30], charcoal water slurries (ChWS) [31], or by dispersing coal/charcoal in oil to obtain coal/charcoal oil slurries (COS/ChOS) [32–42] or in organic solvents such as methanol (CMS), hexanone (CHS), among others [43,44]. The dispersion of coal/charcoal in solvents can be achieved with or without added surfactants. Obtaining a liquid fuel through a slurry-based approach is much simpler and more economically viable in comparison to the use of methods involving liquefaction. This explains the recent upsurge in studies aiming at developing coal-solvent slurries [1], especially in countries where coal reserves are abundant and/or the environmental impact of fuel used must be reduced [1,2]. Coal slurries can be transported, stored and burned in coal boilers without the need to make major changes to the burners [1–4]. However, in order to avoid the occurrence of slagging and fouling phenomena in the boilers, coals with ash contents as little as possible (below 5 wt.%) should be used to prepare the slurries [1,2]. Since the use of coal slurries as fuel implies their transport and storage, the proper design of both the pipelines and the storage systems requires accurate knowledge of slurry rheological behaviour [1,2].

The rheological behaviour of coal slurries is affected by a variety of factors that include: the type of coal [5–9,20]; the type of dispersion media [1–44]; the slurry coal content, which should be ≥55 wt.%, especially for CWS to not compromise the high heating value, and to minimise particle segregation by sedimentation [10]; particle size and particle size distribution, which influence settling and packing

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behaviour [11,12]; the type of surfactants/additives, which can be ionic (cationic/anionic) or non-ionic [13–24]; and the total added amount of surfactants or other processing additives, which should be <1 wt.% and allow viscosity (η) values within the range of 1000–1200 cP (1–1.2 Pa s) at a shear rate ($\dot{\gamma}$) of 100 s^{-1} [13–24].

Dispersing hydrophobic coal particles in oils (to obtain COS) or other organic solvents such as methanol, ethanol or cyclohexanone [32–44] is easier than in aqueous media to prepare CWS. The availability of water as a raw material and the economic and environmental advantages derived from using it as dispersing medium for charcoal, justify its selection in the present work. Furthermore, using water as solvent in coal/charcoal slurries produces less SO_x, CO and NO_x on combustion than a COS/ChOS because of the slightly lower combustion flame temperature [22].

The possibility of using charcoal as an alternative renewable energy source instead of non-renewable fossil fuels appears a very attractive and sustainable option that will help preserving the scarce natural coal and petroleum resources. The increasing demand for petroleum and diesel fuels and their relative scarcity has resulted in an exaggerated increase in their price over the last decade, with charcoal thus appearing as economically attractive [27].

The present work was undertaken to investigate the feasibility of preparing an eco-friendly biofuel from charcoal particles dispersed in water in order to achieve a stable charcoal water slurry (ChWS) with solid loadings >55 wt.%, maximum surfactant contents of 1 wt.%, and exhibiting suitable rheological properties (η within the range of 1–1.2 Pa s at a shear rate ($\dot{\gamma}$) of 100 s^{-1}).

2. Materials and methods

2.1. Charcoal preparation and analyses

The ChWS were prepared from a commercial charcoal supplied by Delgarden (Portugal) and manufactured with an unknown type of biomass. The raw material was pre-ground in a Retsch SM300 cutting mill followed by fine grinding in a Fritsch Pulverizette 6 planetary mill, using ZrO_2 balls as milling media and a charcoal/ZrO_2 balls weight ratio of about 1/5. The ground material was passed through a 250 μm sieve and the passing portion of each batch was stored in a closed box to prevent oxidation and contamination. The ground material accumulated in the box was then homogenised and fully characterised in order to offset the non-existing information regarding the production processes and technical features of the charcoal samples. The following characterisation techniques available in the internal lab of the company YGE were used:

- **Particle size distribution** – A Malvern Mastersizer 3000 was used to determine the PSD.
- **Proximate analysis** – Proximate analysis (TGA), including the determination of charcoal moisture, volatile matter and ash content, was carried out using an ELTRA Thermostep, following ASTM D7582-12.
- **Ultimate analysis** – Charcoal carbon, hydrogen and nitrogen contents were evaluated using a LECO CHN628, following standard operating instructions.
- **High heat value (HHV) and low heat value (LHV)** – A Parr 6400 colorimeter was used to determine the high and low heating values, based on the standards EN 14918 (2009) and EN 15296 (2011) and the equipment's standard operating instructions.

2.2. Preparation and characterisation of charcoal water slurries

ChWS preparation was performed following methods reported in the literature [4–44] for coal slurry fuels and taking into account the available laboratory equipment, with the same systematic procedures employed throughout the entire study in order to enable a comparison of results. The viscosity and rheological behaviour of the slurries were evaluated using a rheometer, Malvern Kinexus Pro$^+$. All characterisation tests were performed according to an internal method established for the particular slurries under study. This method consisted of measuring at room temperature (25 °C) the values of shear stress (τ) and viscosity (η) at the following shear rates ($\dot{\gamma}$): 60, 70, 80, 90, 100, 110, 120, 130, 140 and 150 s^{-1}. The working shear rate was 100 s^{-1} and the viscosity at this shear rate was kept within the range of 1–1.2 Pa s.

The ability of six commercially available surfactants to disperse the charcoal powder in water was investigated aiming at identifying the most effective one. The brand names and suppliers were as follows: Zephrym 4974 and Zephrym 7000, purchased from Croda Europe Limited, Spain; SMA 1440HD from Cray Valley USA and three ligninosulphonates, Borresperse NA, Borresperse MVP and Borrebond FPPI purchased from Borregard, Lignotech Iberica SA, Spain.

Different sets of experiments were carried out in order to identify the most effective surfactant and the maximum content of charcoal allowed by it.

2.2.1. Choosing the surfactant

The charcoal content chosen for this experimental set was 58 wt.% in order to obtain starting slurries with enough viscosity to enable a good discrimination of the relative effectiveness of the six surfactants tested. Increments of 0.1–0.2 wt% surfactant were added to the ChWS in order to evaluate and compare the effectiveness of each surfactant. Liquid Zephrym PD 4974 is a polymeric anionic surfactant commonly used for dispersing inorganic or carbon black in aqueous media. Zephrym PD 7000 (Z7000), also in liquid state, is a polymeric slightly cationic surfactant. It is often used to prepare aqueous systems of carbon black particles. In turn, SMA 1440 HD (SMA) is a non-ionic surfactant based on styrene maleic anhydride copolymer commonly used in pigment dispersions. Ligninosulphonates consist of polymeric anionic surfactants and are known by their high performance in dispersing carbon black in aqueous media. They are also used as dispersants on concrete industry and as deflocculants in cement production. Furthermore, there are some studies about ligninosulphonates in ChWS [5,8,13,14,18,19]. Borresperse NA (B_{NA}), in a powder form, is a sodium ligninosulphonate. Borresperse MVP (B_{MVP}) is a liquid sodium and calcium ligninosulphonate, and Borrebond FPPI (Bb), also in liquid state, is a calcium ligninosulphonate. Based on the dispersion efficacy of these six surfactants, those that allowed the lowest viscosity to be achieved were chosen and used to maximize the charcoal content in the ChWS.

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