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Thermochemical and structural changes in *Jatropha curcas* seed cake during torrefaction for its use as coal co-firing feedstock

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A B S T R A C T

Jatropha curcas seed cake is a viable feedstock for co-firing with coal as it has the advantages of being renewable, carbon-neutral and sourced from a versatile plant. Torrefaction, a mild pyrolysis treatment by heating in a N_2 atmosphere, was investigated as a technique to improve the thermochemical properties of the biomass, primarily the HHV (higher heating value). The temperature and holding time were varied in the ranges of 200–300 °C and 0–60 min, respectively, to form a 5-level full-factorial experimental matrix. An optimum envelope of torrefaction parameters was identified in the range of <5 min at >280 °C to >45 min at 220–250 °C under a heating rate of 10 °C/min. This results in an enhancement of the HHV from 24 MJ/kg to more than 27 MJ/kg, which is within the range of coal, while maintaining an energy yield higher than 90%. The relationships between the HHV and the proximate fixed carbon content as well as the elemental CHO content were also investigated. Through ^{13}C NMR (nuclear magnetic resonance) spectroscopy, hemicellulose was determined as the most volatile component, undergoing decomposition before 250 °C while cellulose only degraded fully in the 250–300 °C range and lignin decomposition spanned from 200 °C to beyond 300 °C.

1. Introduction

The development of alternatives to replace fossil fuels as the primary global energy source is gaining recognition as an issue of utmost importance. The major drivers behind the move away from fossil fuels are emissions releases from fossil fuels combustion and the non-renewable nature of the fuels. The combustion of fossil fuels worldwide generates copious amounts of greenhouse gases in particular carbon dioxide which contribute to global warming. Meanwhile, the non-renewable nature of fossil fuels means that the fuel reserves are finite; some estimates have projected that coal would only last another century [1,2].

Among the various alternative energy technologies, biomass co-firing stands out since it allows for the use of existing infrastructure without extensive modifications. Biomass in itself has the advantages over fossil fuels of being relatively carbon-neutral over the entire life cycle and also being renewable if sourced from sustainable plantations. Biomass co-firing with coal provides an immediate and practical solution to mitigating coal usage since coal plants of several hundred MW can be utilised in contrast to the 20–100 MW capacity of current biomass-only plants; the initial capital costs of building new plants are also avoided and biomass co-firing is considered one of the least costly alternative energy sources [3,4]. Co-firing also has the added advantage over coal of having enhanced ignition characteristics [5], and the flexibility over biomass-only plants of being less affected by seasonal availability of biomass [6].

There is a large variation in properties within the different types of biomass, and these can also vary widely from those of coal. It is this variation that is responsible for the technical constraints on co-firing. Closing this gap between the properties would diminish the need for specialised handling and combustion equipment, and would allow a higher proportion of biomass to be used in the co-firing blend [7]. The properties in question are thermochemical as well as physical – biomass has a higher moisture content, lower energy density and different grindability characteristics compared to coal [8–10].

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Therefore, it is imperative to investigate pre-treatment techniques which would overcome some of the unfavourable characteristics of biomass and hence bring its behaviour closer to that of coal. One such technique is torrefaction, which involves a non-combustive mild pyrolysis reaction which occurs when the biomass is heated in an inert atmosphere (typically N_2) to a temperature between 200 °C and 300 °C [11]. Torrefaction increases the calorific value of the biomass, and this is one of most important benchmarks of the process; this in turn has a positive effect on the energy density of the biomass [12]. The process inevitably reduces the moisture content of the fuel, but also has the effect of making it more hydrophobic, i.e. its susceptibility to absorb moisture is reduced [13,14]. In addition to this, torrefaction has been shown to alleviate the poor grindability of biomass, which is an important outcome since it allows a uniform particle size distribution in the coal-biomass blend to be attained using existing milling/handling systems [15,16].

Jatropha curcas or *J. curcas* is a species of shrub which is gaining recognition as a potential source of renewable energy in the form of biodiesel, as evidenced by the increasing number of *Jatropha* plantations that have been set up in (sub)tropical regions worldwide for this purpose [17]. The plant has a number of features that make it an appealing proposition as a bioresource – it can grow in annual rainfall conditions up to 1500 mm, is able to withstand extended periods of drought [18] and is resistant to most pests [19], as well as grows and propagates rapidly [20]. Furthermore, its toxicity ensures a lack of competition with the food industry, which is an issue faced by sources of bioenergy such as palm oil and sugar cane [21]. Due to its adaptability to tropical and arid conditions, it is found natively and in plantations in Central America, Africa, India, China and Southeast Asia [22].

The primary driver behind current interest in *J. curcas* is biodiesel production using the oil from the seeds. To date, there have been many studies on the utilisation of *J. curcas* oil as biodiesel feedstock. However, the oil content of the seed is typically less than 40%, and only 60–80% of this is extracted using conventional mechanical methods [23–25]. It follows then that the solid residue left after oil extraction (seed cake) still amounts to a significant amount of biomass, and a useful quantity of bioenergy could potentially be extracted from this waste product via co-firing. Nevertheless, co-firing of this seed cake is liable to the aforementioned complications due to potential differences in properties with coal.

There is a substantial gap in the research with respect to comprehensive characterisation, subsequent pre-treatment and evaluation of *J. curcas* seed cake as a viable feedstock for combustion and/or co-firing. With the increasing recognition of *J. curcas* seed oil as a viable biodiesel feedstock, an investigation into utilising the resulting seed cake in this manner would be a worthwhile undertaking. This study investigates the upgrading of certain fuel properties of *J. curcas* seed cake via torrefaction, to increase its viability for co-firing. In addition to the thermochemical changes such as the proximate and ultimate composition and HHV (higher heating value), ^{13}C NMR (nuclear magnetic resonance) spectroscopy is used to investigate the structural changes taking place during the torrefaction process.

2. Materials and methods

2.1. Material

J. curcas seeds were provided by ACGT Sdn. Bhd. (Malaysia). They were dried for 24 h in an oven at 105 °C, and double wrapped in large plastic bags before shipping to Nottingham, UK. 55 kg of the seeds were sent to an external facility (Statfold Seed Oil Ltd.) for oil extraction using an expeller press. 48.5 kg of solid residue (seed cake) were obtained, corresponding to an oil yield of 12%. This is lower than the oil yield of 28–40% reported in the literature [19,26,27]. The seed cake appeared to consist of two distinct components – hard, dark, rod-like structures in a soft, oily, loose soil-like matrix. The latter comprised approximately ¾ by weight of the total seed cake, and was the primary focus of this study.

2.2. Torrefaction experimental matrix

A 5-level full-factorial (triplicated) design of experiment was used. The tested torrefaction temperatures were 200 °C, 225 °C, 250 °C, 275 °C and 300 °C, while the tested holding times used were 0 min, 15 min, 30 min, 45 min and 60 min. The run order was randomised using Minitab 17 statistical software, which was also used for the subsequent data analysis. Including the replicates, a total of 75 torrefaction runs were carried out.

2.3. Torrefaction methodology

Torrefaction of the seed cake was carried out using a HTF (horizontal tube furnace). The HTF used was a TSHH 11/90/457 model manufactured by Elite Thermal Systems. It is a split-type furnace with a tube diameter of 90 mm and a heated zone length of 457 mm, which can reach a maximum temperature of 1100 °C. A quartz reactor tube with an internal diameter of 60 mm was placed within the furnace. End seals were fitted to the two open ends of the reactor tube, and a N_2 gas supply was connected to one end. A rotameter enabled the gas flow rate to be controlled.

For each torrefaction run, 25 g (±0.5 g) was measured into a ceramic "weighing boat". The weighing boat was placed in the middle of the reactor tube and both ends of the tube were sealed using rubber bungs. The N_2 supply was switched on and set to 2 L/min. After the N_2 flow had been running for 5 min (to ensure that O_2 is purged out of the reactor tube), the furnace was switched on. For each run, a constant ramp of 10 °C/min was used until the required torrefaction temperature was reached, followed by an isothermal period for the necessary holding time.

Immediately after the run was completed, the controller switches off the furnace and the hood of the furnace was opened to accelerate cooling. When the temperature readout reached 100 °C, the N_2 supply was switched off and the sample was removed from the reactor tube. The sample was reweighed after it had cooled down to room temperature, and transferred to an airtight plastic bag for storage until subsequent analyses were carried out. The post-run procedure was standardised across all runs regardless of torrefaction temperature and holding time, since the pyrolysis process would continue to occur at the elevated temperatures during the cooling phase.

The mass yield following each torrefaction run was calculated using Eq. (1).

$$mass\ yield = \frac{final\ mass}{initial\ mass} \times 100\% \quad (1)$$

2.4. Proximate analysis

TGA (thermogravimetric analysis) was used to determine the proximate composition of the seed cake, i.e. the moisture, VM (volatile matter), FC (fixed carbon) and ash content. The fundamental concept behind this technique is that the biomass sample undergoes mass loss in several consecutive stages as it is heated. These stages correspond to the different proximate components of the biomass being lost (moisture, VM, FC in that order), with the