Department of Chemical Engineering

High Energy Density Fuels Derived from Mallee Biomass: Fuel Properties and Implications

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ABSTRACT

Mallee biomass is considered to be a second-generation renewable feedstock in Australia and will play an important role in bioenergy development in Australia. Its production is of large-scale, low cost, small carbon footprint and high energy efficiency. However, biomass as a direct fuel is widely dispersed, bulky, fibrous and of high moisture content and low energy density. High logistic cost, poor grindability and mismatch of fuel property with coal are some of the key issues that impede biomass utilisation for power generation. Therefore, innovations are in urgent need to improve biomass volumetric energy densification, grindability and good fuel matching if co-fired with coal. Biomass pyrolysis is a flexible and low-cost approach that can be deployed for this purpose. Via pyrolysis, the bulky biomass can be converted to biomass-derived high-energy-density fuels such as biochar and/or bio-oil. So far there has been a lack of fundamental understanding of mallee biomass pyrolysis and properties of the fuel products.

The series of study in this PhD thesis aims to investigate the production of such high-energy-density fuels obtained from mallee pyrolysis and to obtain some new knowledge on properties of the resultant fuels and their implications to practical applications. Particularly, the research has been designed and carried out to use pyrolysis as a pretreatment technology for the production of biochar, bio-oil and bioslurry fuels. The main outcomes of this study are summarised as follows.

Firstly, biochars were produced from the pyrolysis of centimetre-sized particles of mallee wood at 300-500°C using a fixed-bed reactor under slow-heating conditions. The data show that at pyrolysis temperatures > 320°C, biochar as a fuel has similar fuel H/C and O/C ratios compared to Collie coal which is the only coal being mined in WA. Converting biomass to biochar leads to a substantial increase in fuel mass energy density from ~10 GJ/tonne of green biomass to ~28 GJ/tonne of biochars prepared from pyrolysis at 320°C, in comparison to 26 GJ/tonne for Collie coal. However, there is little improvement in fuel volumetric energy density, which is still around 7-9 GJ/m^3 in comparison to 17 GJ/m^3 of Collie coal. Biochars are still bulky and grinding is required for volumetric energy densification. Biochar grindability experiments have shown that the fuel grindability increases drastically even at pyrolysis temperature as low as 300°C. Further increase in pyrolysis temperature to 500°C leads to only small increase in biochar grindability. Under the grinding conditions, a significant size reduction (34-66 % cumulative volumetric size <75 μm) of biochars can be achieved within 4 minutes grinding (in comparison to only 19% for biomass after 15 minutes grinding), leading to a significant increase in volumetric energy density (e.g. from ~8 to ~19 GJ/m^3 for biochar prepared from pyrolysis at 400°C). Whereas grinding raw biomass typically result in large and fibrous particles, grinding biochar produce short and round particles highly favourable for fuel applications.

Secondly, it is found that the pyrolysis of different biomass components produced biochars with distinct characteristics, largely because of the differences in the biological structure of these components. Leaf biochars showed the poorest grindability due to the presence of abundant tough oil glands in leaf. Even for the biochar prepared from the pyrolysis of leaf at 800°C, the oil gland enclosures remained largely intact after grinding. Biochars produced from leaf, bark and wood components also have significant differences in ash properties. Even with low ash content, wood biochars have low Si/K and Ca/K ratios, suggesting these biochars may have a high slagging propensity in comparison to bark and leaf biochars.

Thirdly, bio-oil and biochar were also produced from pyrolysis of micron-size wood particle using a fluidised-bed reactor system under fast-heating conditions. The excellent grindability of biochar had enabled desirable particle size reduction of biochar into fine particles which can be suspended into bio-oil for the preparation of bioslurry fuels. The data have demonstrated that bioslurry fuels have desired fuel and rheological characteristics that met the requirements for combustion and gasification applications. Depending on biochar loading, the volumetric energy density of bioslurry is up to 23.2 GJ/m^3, achieving a significant energy densification (by a factor > 4) in comparison to green wood chips. Bioslurry fuels with high biochar concentrations (11-20 wt%) showed non-Newtonian characteristics with pseudoplastic behaviour. The flow behaviour index, *n* decreases with the increasing of biochar concentration. Bioslurry with higher biochar concentrations has also demonstrated thixotropic behaviour. The bioslurry fuels also have low viscosity (<453 mPa.s) and are pumpable at both room and elevated temperatures. The concentrations of Ca, K, N and S in bioslurry are below the limits of slurry fuel guidelines.

Fourthly, bio-oil is extracted using biodiesel to produce two fractions, a biodiesel-rich fraction (also referred as bio-oil/biodiesel blend) and a bio-oil rich fraction. The results has shown that the compounds (mainly phenolic) extracted from bio-oil into the biodiesel-rich fraction reduces the surface tension of the resulted biodiesel/bio-oil blends that are known as potential liquid transport fuels. The bio-oil rich fraction is mixed with ground biochar to produce a bioslurry fuel. It is found that bioslurry fuels with 10% and 20% biochar loading prepared from the bio-oil rich fraction of biodiesel extraction at a biodiesel to bio-oil blend ratio 0.67 have similar fuel properties (e.g. density, surface tension, volumetric energy density and stability) in comparison to those prepared using the original whole bio-oil. The slurry fuels have exhibited non-Newtonian with pseudoplastic characteristics and good pumpability desirable for fuel handling. The viscoelastic behaviour of the slurry fuels also has shown dominantly fluid-like behaviour in the linear viscoelastic region therefore favourable for atomization in practical applications. This study proposes a new bio-oil utilisation strategy via coproduction of a biodiesel/bio-oil blend and a bioslurry fuel. The biodiesel/bio-oil blend utilises a proportion of bio-oil compounds (relatively high value small volume) as a liquid transportation fuel. The bioslurry fuel is prepared by mixing the rest low-quality bio-oil rich fractions (relatively low value and high volume) with ground biochar, suitable for stationary applications such as combustion and gasification.

Overall, the present research has generated valuable data, knowledge and fundamental understanding on advanced fuels from mallee biomass using pyrolysis as a pre-treatment step. The flexibility of pyrolysis process enables conversion of bulky, low fuel quality mallee biomass to biofuels of high volumetric energy density favourable to reduce logistic cost associated with direct use of biomass. The significance structural, fuel and ash properties differences among various mallee biomass components were also revealed. The production of bioslurry fuels as a mixture of bio-oil and biochar is not only to further enhance the transportability/handling of mallee biomass but most importantly the slurry quality highly matched requirements in stationary applications such as combustion and gasification. The co-production of bioslurry with bio-oil/biodiesel extraction was firstly reported in this field. Such a new strategy, which uses high-quality extractable bio-oil compounds into bio-oil/biodiesel blend as a liquid transportation fuel and utilises the low-quality bio-oil rich fraction left after extraction for bioslurry preparation, offers significant benefits for optimised use of bio-oil.

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