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Full Length Article

Global kinetics of the rate of volatile release from biomasses in comparison to coal

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ABSTRACT

The chemistry involved in the propagation of pulverised biomass flames is not well understood. All biomass fuels release volatiles at a much lower temperature than coal and the proportion of volatiles is much greater than for coal, typically 80% compared to 30%. Thus, the rate of release of volatiles from biomass fuels is much more important in the pulverised fuel flame propagation than it is for coal, where the rate of char oxidation is more important. The rate of release of volatiles from dry biomass follows three stages: the first stage for typically 10% of the volatiles occurs over 200–300 °C, the second stage of about 70% of the total volatile mass occurs over the temperature range 300–400 °C. Finally, there is a slow loss of volatiles, accounting for remaining 20% of volatiles, over the temperature range 400–900 °C. Stagg's quick approximation method was used to determine the kinetics for the rate of volatile yield. Biomass samples were found to have lower activation energies and higher rate of release of volatiles in comparison with coal samples, up to 300–400 °C. Similar release rates were found for the 3rd stage of volatile release. The release of volatiles at low temperatures potentially makes the biomass pulverised fuel more reactive and one consequence is shown in the measurement of minimum explosion concentration, MEC. A good correlation was found between activation energies and the MEC, determined on the Hartmann equipment. There is currently little understanding of the composition of the volatiles released at low temperatures from biomass, as most publications are for pyrolysis conditions at high temperature. It is possible that the volatiles are a mixture of mainly H_2, CO and CH_4 and the likely proportions of these were calculated from the elemental and thermo-gravimetric analysis. This was done for a range of biomasses and this showed that the most important volatile gas is likely to be CO and that CH_4 yield is very low. This means that the conventional model used in coal combustion of char plus methane combustion is not applicable to biomass combustion.

1. Introduction

Pulverised biomass combustion in existing pulverised coal power stations is one of the most cost effective routes to greenhouse gas (GHG) reductions in electric power supply. In 2014 5.8% of the UK's supplied electricity was generated from pulverised biomass mainly used in existing coal fired power stations [1]. This was a 25.7% increase on 2013 and in 2014 was 19.69 Mtoe [1]. It was the fastest growing renewable electricity source between 2013 and 2014. In spite of its growing use, the mechanism of combustion of pulverised biomass has received relatively little study. The properties of biomass are quite different from those of coal and these will result in different burning mechanism. Perhaps the greatest difference between the two fuels is the much higher proportion of volatile matter in biomass. The rate at which volatiles are released from biomass and the global kinetics of this volatile release are studied in the present work, with the aim that the global kinetics can be incorporated into CFD modelling of biomass combustion.

Biomass fuels have a lower bulk density, higher volatile content, lower calorific value and higher moisture content than coal and a greater fire and explosion risk [2,3]. Woody biomass fuels have a more variable composition than coal [4–10] and they are also more difficult to mill due to their fibrous structure.

A wide range of biomass sources from wood to agricultural wastes are studied in the present work, some of which were supplied in pellet form but were crushed to extract the original pulverised biomass. The agricultural biomass was milled and sieved in the laboratory. A characteristic of biomass is its fibrous

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Nomenclature

A	pre-exponential factor
A/F	area to fuel ratio
CV	calorific value (MJ/kg)
daf	dry ash free basis
dm/dt	rate of normalised volatile loss
dP/dt	rate of pressure rise (bar/s)
E	activation energy (kJ/mol)
FC	fixed carbon (%)
GHG	greenhouse gas
HC	hydrocabon
k	rate constant
LFL	lean flammability limit
m	normalised volatile yield
MEC	minimum explosible concentration
Mtoe	million tonnes of oil equivalent
T_A	activation temperature
T_c	characteristic temperature
ΔT_c	characteristic temperature range
T_S	solid material temperature
VF	volatile fraction
VM	volatile matter (%)

Special characters

ϕ	equivalence ratio

structure, which makes biomass difficult to mill in equipment designed for the milling of brittle coal.

Thermally treating the biomass by heating at around 260–320 °C, is a process known as torrefaction. This causes (among other changes) the biomass to become brittle and easier to mill. An alternative thermal treatment process that also destroys the fibrous structure is "steam-explosion" treatment which involves heating to similar temperatures with hot steam at high pressure and then releasing this pressure so that the water absorbed in the biomass 'explodes' out shattering the biomass. Steam exploded biomass is often referred to as 'black pellets' as the final fuel pellets are black. Both types of thermally treated biomass were included in the present study for comparison. The parent wood was yellow pine and this is also included in the study [11].

The high volatile content of biomass and thermally treated biomass and its ease of release make biomass more reactive than coal. One measure of this increased reactivity is the lean flammability limit or minimum explosion concentration (MEC) [4] and this was the method used in the present work using the Hartmann dust explosion equipment. This equipment was modified to enable the flame propagation speed (another reactivity parameter) to be determined.

The high reactivity of biomass is also shown in the large number of explosion and fire incidents in pulverised biomass production, storage and utilisation in power plants. Many biomass fire/explosion incidents have occurred in the past and are still happening [4,12]. The detailed investigations of these biofuels need to be assessed properly before their adoption and retrofitting of the plants [5,6]. The present work gives both reactivity information in the form of the rate of volatile release and the MEC.

Biomasses are more reactive and have different chemical characterisation than coal [7,8]. They have higher volatile yield and lower fixed carbon content compared to coals [9,10]. The adoption of biomass as a partial or complete replacement for coal requires the measurement of the chemical and physical properties and the chemistry involved in their conversion. Particle size and the heating rates greatly affect the rate of release of volatiles due to the thermal inertia of the particles. The rate of release of volatiles is a critical parameter for the stability of the pulverised fuel flames on burners.

It has been observed that decreasing the particle size and increasing the heating rate results in an increase in the rate of release of volatiles up to a critical point [9,10]. It was observed that biofuels of coarse particle size range of 300–500 µm were still explosible in contrast to coals of similar particle size [13–16]. Woody biomasses showed a decrease in the MEC with a decrease in particles size. However, the ash derived crop residues when milled enriched the finer fraction with more ash contents. The enhanced yield of ash in the finer fraction acts as an inert and counterbalances the effect of particle size on the lean flammability limit [13].

The minimum explosive concentrations of the biomasses are found to be much leaner than for coal and even hydrocarbon gases in terms of equivalence ratio [3,13,15,17–20]. Most of the data on the MEC in the literature are expressed in terms of g/m^3, which when converted to equivalence ratio helps to compare the results with equivalent LEL data for other fuels [21]. Most hydrocarbon fuels have their lean flammability limits at half of their stoichiometric concentration. Oxygenated fuels such as biomass were found to have their MEC much leaner than the LEL for gaseous hydrocarbons [3,13,15,17–21]. It was also observed that coal and biomass fuels have no upper flammability limit. Deguingand and Galant [22] employed weak spark ignition for the determination of the upper flammable limit and found apparent upper flammable limit of coal dust to be ∼4 kg/m^3, which is more an ignitability limit rather than a flammability limit because of the weak ignition source. Wolanski [23] found that increasing the concentration reduces the flame temperature below its limit value and also observed that the dusts do not have upper flammability limit.

The kinetics for volatile yield and their chemical characterisation will help to understand the mechanism of flame propagation in pulverised biomass. A range of biomass samples including woody and agricultural biomass were investigated for the release of volatiles using thermal gravimetric analysis (TGA) and their devolatilisation kinetics were derived using Stagg's [24–26] quick approximation method. Two different models, as developed by Staggs [24–26], were applied for the kinetic study of these biomasses: Series Reaction Model and Competitive Reaction Model.

2. Experimental techniques

The elemental analysis of biomass and coal used a Flash 2000 Thermo Scientific Analyser. It consists of a single reactor with temperature of 1800 °C for the detection of Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) with O found by subtracting the mass of CHNS from the original mass. At this extreme temperature, the material is converted into carbon dioxide, water, nitric oxides and sulphur oxides. These combustion products are separated by a chromatographic column and detected using a Thermal Conductivity Detector (TCD).

Proximate analysis (water content, volatile matter, fixed carbon and ash) was carried out using a Shimadzu TGA-50 thermogravimetric analyzer. It consists of a mass balance attached to a ceramic sample pan in a furnace. It records the weight loss with