Kinetic parameters of the intrinsic reactivity of woody biomass and coal chars via thermogravimetric analysis

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ABSTRACT

The available data on intrinsic kinetic parameters of wood char combustion is limited in the literature. The intrinsic reactivity of porous char particles reflects the variance in the pore structure resulted from various compositions of parent biomass or coal fuels. In this study detailed kinetic models for calculating the intrinsic reaction rate and the Arrhenius parameters in two combustion zones are developed for the char combustion. The influence of the parent fuel composition and the thermal treatment on the char oxidative reactivity observed on the char surface area and particle density are explored through a mathematical model of the char service area and density. A higher reactivity of the wood pellets than coal and enhanced reactivity with the increasing pyrolysis temperature were observed as well.

1. Introduction

The combustion of solid fuel particles is a complex series of sequential and simultaneous reactions that can be classified in two major steps. The first step is the devolatilization of hydrocarbons and oxygen radicals (pyrolysis), supplemented by a profound change in the particle structure. The second step is the combustion of the solid porous residue (char) generated in the first step [1,2].

Researchers have examined the biomass devolatilization products and many have developed reactivity models to calculate the kinetic parameters based on the three components classification (cellulose, hemicellulose and lignin). Biomass pyrolysis was described to a certain acceptable extent by a global irreversible first-order reaction, and the devolatilization rate is only a function of temperature [3–5]. However, the reaction can be demonstrated by more than one step and combines various species reactions. Agrawal [6] and Conesa et al. [7] found that the model proposed by Kilzer and Broido [8] (KBM) of wood pyrolysis had the best fitting with the TGA experimental data. The KBM assumes a sequence of reaction steps starting with the formation of anhydrocellulose (Ce*) and tar then the intermediate Ce* decomposes into volatiles and char. Mania et al. [9], Branca et al. [10], and Martin-Lara et al. [11] assumed three parallel non-interactive decomposition reactions of the three components (cellulose, hemicellulose and lignin) in sugarcane bagasse and waste wood with a first-order model for hemicellulose and cellulose, and a third-order model for lignin. However, it was found that Lignin decomposes at a wide range of temperatures that overlap with the other components [12].

The char reactivity is an imperative parameter of the simulation and process design of the combustion process due to the major contribution of the char oxidation to the heat value of the fuel. There are many rate law models used to explain the char combustion in the literature. The char combustion data were treated with Arrhenius model as a global n-order reaction of the oxygen pressure [13–17].

For the combustion of porous carbon particles, Essenhigh [18], assumes that the complex reaction occurs in a sequence of steps starting with the diffusion of oxygen through the stagnant boundary layer of nitrogen outside the particle to reach the external surface of the particle, chemisorption of oxygen on the external surface of the particle, internal (pore) diffusion, then further reaction of the remaining oxygen and carbon, and finally the diffusional discharge of the reaction products. The char is assumed a uniform sphere of carbon, and the reaction rate is the mass of carbon consumed per unit area, and proportional to the oxygen pressure. He represents the reaction rate as follows:

$$R_A = -\rho_p \cdot \frac{dr}{dt} = -k \cdot P_{O2} \tag{1}$$

where;

R_A: is the reaction rate, kg·m^{-2}·s^{-1}
r: is the particle radius, (m)
ρ_p: is the particle density, (kg·m^{-3})
k: is the specific reaction rate coefficient, (s^{-1})
P_{O2}: is the oxygen pressure, (kg·m^{-2}

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The Langmuir-Hinshelwood rate expression, assumes that the reaction rate is controlled by two kinetic mechanisms, first is a non-dissociative adsorption of oxygen particles on the carbon surface to form the complex C(O), and the second step is the desorption of C(O) [13,19,20] .

$$C + O_2 \rightarrow C(O) \tag{2}$$

$$C(O) \rightarrow CO \tag{3}$$

In 2001, Hurt found that both the single step global model and the Langmuir-Hinshelwood model do not describe the reaction order data of char combustion [20]. Observations of CO_2 forming in the reaction suggested the reaction of gaseous oxygen with the complex C(O) as an intermediate step [21,22]

$$C + O_2 \rightarrow C(O) \tag{4}$$

$$C(O) + O_2 \rightarrow CO_2 + C(O) \tag{5}$$

$$C(O) \rightarrow CO \tag{6}$$
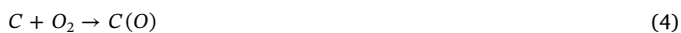
Thermal treatment of biomass and coal via a thermogravimetric analysis (TGA) has been extensively used to study the solid-phase burn-out rate [15,21,23–28]. Still, the intrinsic reactivity of biomass char combustion in comparison to coal has not gained enough interest and investigations in the literature. Also, the effect of the ash content on the pore surface area is not intensively highlighted in research work [29]. The intrinsic reactivity is the reaction rate per unit of total internal pore surface area per unit pressure of oxygen in the absence of any mass transfer limitations [30,31].

In 1972, Smith & Tylor [32] have formulated the relation between the apparent rate of reaction and the intrinsic reactivity for a first-order irreversible reaction of a porous solid as follows:

$$R_{ac} = \eta \ddot{R}_s A_g \rho_a \gamma \tag{7}$$

where;

η: effectiveness factor (η < 1).

It represents the actual chemical reaction rate as a fraction of the maximum rate possible on the total internal surface area of the particle [33]

In char combustion it is the fraction of the specific internal surface area A_g necessary for reaction if the local intrinsic rate was identical to $\ddot{R}$ [31].

$\ddot{R}$: Intrinsic rate for the hetrogeneous char reaction, (kg carbon·m^{-2}·s^{-1})

A_g: Specific pore internal surface area, (m^2·kg^{-1})

ρ_a: appearant particle density, (kg·m^{-3})

γ: the ratio between particle volume to particle surface area, (m)

Then, Smith [2,30], and Laurendeau [31] have given the details of calculating the effectiveness factor from the Thiel modulus ϕ for first and n-order reactions of porous solids.

Eq. (7) has been widely used in the modelling of coal char combustion and gasification in literature [34–39]. Adanez et al. [40] used the TGA data to predict the intrinsic kinetic parameters of wood chars and applied the kinetic parameters on the fluidized bed combustion boilers. Recently, Gao et al. [41] used the random pore model (RPM) to calculate the intrinsic reactivity of rice husk char gasification with CO_2. They determined the intrinsic reaction rate constant as a function of the gasification temperature and the oxidant partial pressure. However, they assumed that gasification of the char at 950 °C is in the combustion zone I where there is no diffusion limitation. Therefore, they did not consider the effectiveness factor in the determination of the intrinsic reactivity. This assumption at such a high temperature does not comply with all the published data on combustion zone I that are reviewed by Smith [2].

The intrinsic reactivity of a char depends on three elements; 1.

Concentration of edge carbon atoms and dislocations, 2-mineral matter and trace elements, and 3- oxygen and hydrogen contents [31]. The overall reactivity also depends on the char porosity [42]. In addition, the char preparation conditions, i.e. heating rate, final pyrolysis temperature, and the residence time of the pyrolysis step, have a great effect on the produced char reactivity [43,44]. The pyrolysis at low temperatures increases macropore size and decreases in the micro and mesoporous due to re-polymerization, particularly for plasticizing bituminous coals (high volatile matter content), and therefore increases the specific surface area of the char. While at higher pyrolysis temperatures the structural carbon crystallization increases, thus resulting in a lower concentration of the active sites [42,43]. Similar conclusions were reached for anthracite coal due to the graphitization [45], and for sub-bituminous coal [46] due to the microporous blockage. Moreover, the char density increases with the increase of the heat-treatment temp [47].

The work of this paper aims to evaluate the thermal behaviour of biomass at various devolatilization temperatures, and the reactivity of the biomass char combustion in comparison to coal. In addition, the intrinsic kinetic parameters and reactivity of the biomass char combustion are determined and evaluated in comparison to coal. Furthermore, the effect of the char preparation conditions, parent fuel composition, and ash content on the char reactivity are also investigated. Non-isothermal TGA data are used in the pyrolysis stage with the aim of producing chars at a certain temperature and burn them isothermally. Multiple sets of experiments are performed to produce char at different temperatures.

2. Materials & experimental methods

Two types of wood pellets and two coal samples are used in this comparison. The biomass samples are the milled US white wood pellets (USWWP) imported by a power company in 2015, and the Canadian milled wood pellets (CAWWP) imported by E-ON company in 2014. Both are mainly produced from soft wood parts such as spruce, fir and pine. The two coal samples used in this comparison are one from Vietnam-Hon gai region, which is infrequently studied in the literature (VC) and the other one is the Colombian coal El Cerrijon origin (ELC). These two types are the regularly imported types of coal to the UK.

The proximate analysis measurements on as received (ar) fuels were performed according to the BSI standard methods BS EN ISO 18122, BS EN ISO 18123, and BS EN ISO 18134-1 using a Carbolite LHT6/30 furnace for ash content analysis and a Carbolite muffle furnace SCF 1100 for volatile matter content. The ultimate analysis on dry-ash-free (daf) basis, was performed with a Perkin Elmer flash2000 elemental analyser according to the BSI standard method BS ENISO 16948 to determine the C, H, N, S of each sample. The proximate and ultimate analysis of the samples are given in Table 1. In contrast to the other three samples, the VC sample shows a significantly high ash content at 38.25% wt. The influence of this high percentage in ash content on the char reactivity is intensely discussed in this paper.

2.1. Sample preparation for TGA

Samples of 10 g were oven dried at 105 °C for 4 hours and the weight is checked after the third hour every 20 minutes to ensure a constant weight is obtained. Then the samples are cooled in a desiccator and crushed in a mortar and pestle to homogenise them for sieving to less than 80 μm particles, and stored in sealed containers for further analysis. The published studies have shown that in TGA experiments, the pulverized coal or biomass are within the particle size 63–100 μm [2,47–50]. The small particle size is necessary for the TGA testing to ensure uniform heat distribution and gas diffusion within the sample particles, and to eliminate the effect of particle size on the rate of pyrolysis [51]. 5 mg ± 5% of each fuel type were used in the TGA tests to achieve consistency and uniform heat transfer throughout the sample particles.