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Characterization of high-temperature rapid char oxidation of raw and torrefied biomass fuels

Jun Li [a,*], Giorgio Bonvicini [b], Enrico Biagini [c], Weihong Yang [a], Leonardo Tognotti [b,c]

[a] Division of Energy and Furnace Technology, Royal Institute of Technology (KTH), Brinellvägen 23, 10044 Stockholm, Sweden
[b] International Flame Research Foundation (IFRF), Via Salvatore Orlando 5, 57123 Livorno, Italy
[c] Dipartimento di Ingegneria Civile e Industriale, Università di Pisa, Largo Lucio Lazzarino, 56122 Pisa, Italy

HIGHLIGHTS

- The char oxidations of two biomass chars were tested in an Isothermal Plug Flow Reactor.
- Reactivity of raw biomass char is compared with that of torrefied biomass char.
- The char oxidation kinetic parameters are determined using a parameter optimization method.
- Determined kinetics are examined by comparing the experimental and predicted mass conversions.

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ABSTRACT

The promising properties of torrefied biomass provide a valid co-firing option for large percentage biomass utilization in existing coal-fired boilers. Torrefied biomass is expected to have a better combustion stability than raw biomass and similar to that of coal. The present work will characterizes the oxidation properties of torrefied biomass char and compare with that of raw biomass char. The studied two chars are produced from raw and torrefied biomass in an Isothermal Plug Flow Reactor (IPFR) at high temperature and high heating rate, a sufficient residence time is applied for the completion of the high temperature devolatilization. Char oxidation tests are carried out in the IPFR by varying temperature, oxygen concentration and residence time. The reactivity of two studied chars are analyzed and compared with referenced biomass char and coal char, and the impact of torrefaction on char reactivity is also discussed in this paper. Finally, the char oxidation kinetic parameters are determined using a parameter optimization method, and the obtained kinetics are examined by comparing the experimental and predicted mass conversions.

1. Introduction

The handling and combustion characteristics of biomass can be substantially improved through torrefaction [1]. The promising properties of torrefied biomass provide a co-utilization option incorporating large percentage biomass co-firing ratio in existing coal-fired boilers without major modifications. Accordingly, a torrefaction based co-firing system in pulverized coal boilers has been proposed toward the goal of a 100% fuel switch [2].

When the biomass particles enter a pulverized fuel flame, they are rapidly heated to a final temperature in the range of 1400–1600 °C at a rate of about 10^4 °C/s [3]. The study of the char oxidation kinetics of biomass obtained at the high temperatures and high heating rates is very limited. Lin et al. [4] proposed an aerosol-based method to characterize particles fragmented from biomass chars during oxidation at high temperatures, and the oxidation of char particles in the reactor was investigated by determining on-line the particle size distributions before and after the passage through the reactor. Campbell et al. [5] characterized coal and biomass char at high temperatures using a heterogeneous reaction mechanism that not only describes the variations in char reactivity with conversion at low temperatures but also predicts high enough reaction rates at high temperatures to yield the mass loss rates observed in a laminar flow reactor, their results indicate that the char intrinsic reactivity decreases progressively during oxidation at high temperatures. Jiménez et al. [6] performed devolatilization and combustion experiments of pulverized biomass in an entrained flow reactor under realistic combustion conditions, to derive the kinetic parameters that can be used in

* Corresponding author at: Systems, Power & Energy Research Division, School of Engineering, University of Glasgow, Glasgow G12 8QQ, UK. Tel.: +44 (0)141 330 4327.
E-mail addresses: jun2@kth.se, jun.li@glasgow.ac.uk (J. Li).

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Nomenclature

Symbols
- A pre-exponential factor in Arrhenius expression (1/s)
- C diffusion constant 5×10^{-12}(m^2/s)
- D diffusion rate coefficient (m^2/s)
- d_p particle diameter (m)
- E activation energy (J/kmol)
- k kinetic constant (kg/m^2 Pa s)
- m mass (kg)
- n reaction order (–)
- P pressure (Pa)
- R gas universal constant 8.3143 J/(mol K)
- S char specific surface (m^2/kg)
- T temperature (K)
- X mass conversion (–)
- α particle size evolution exponent (–)

Abbreviations
- ash ash content of residue ($\%_{db}$)
- daf dry ash free basis
- db dry basis
- FC fixed carbon content
- IPFR Isothermal Plug Flow Reactor
- MC moisture content
- PKS palm kernel shell, the parent material of torrefied biomasses
- RB raw biomass, in this work RB refers PKS
- RSME root square mean error
- TB torrefied biomass (PKS after 30 min torrefaction at 300 °C)
- VM volatile matters

Subscripts
- 0 initial value
- ∞ bulk gas
- exp experimental
- g gas phase
- mod modeled
- p particle
- s surface

particle combustion model with good fitting the observed behaviors. However, in general, there is still lack of a work that investigates and compares the char reactivity before and after torrefaction under real combustion conditions.

Tapasvi et al. [7] characterized the combustion behavior of four torrefied wood samples and parent feedstock (birch and spruce) at slow heating programs by thermogravimetric analysis (TGA), and the experimental data was used for the kinetic evaluation. Fisher et al. [8] performed TGA to study the char reactivity of raw and torrefied biomass in O_2 and steam atmospheres; the studied chars were prepared from torrefied and raw willow under both high- and low-heating-rate conditions and it was concluded that torrefaction consistently reduces char reactivity. Arias et al. [9] carried out TGA on raw and torrefied biomass to study their reactivity, and the torrefaction process was found to influence the parameters at the first stage, whereas those corresponding to the second remained unaffected. An analysis based on TGA could be employed to generally understand the char reactivity, but mass and heat transfer limitations make it impossible to determine the accurate kinetics by using TGA methods [4,10], due to the relatively low temperatures (<1000 °C) and low heating rate (<1 °C/s).

Torrefied biomass is supposed to be a coal-like fuel used in industrial furnaces, and thus its combustion performance is expected similar to that of coal. In our previous paper [11], high-temperature rapid devolatilization of biomasses with varying degrees of torrefaction have been investigated, concluding that biomass decreases its reactivity after torrefaction, and the deeper the torrefaction degree, the lower is biomass reactivity. During the combustion process of biomass, the rate of char oxidation is slower than biomass thermal decomposition and volatiles combustion [12]. Accordingly, the rate of char oxidation determines the overall combustion process, and a good understanding of the reactivity of biomass char becomes more important for the biomass combustion process. Compared to the char produced at low heating rate, a more reactive char is produced after devolatilization at high heating rates, associating with larger pores and larger total surface area [12]. Also Biagini et al. [13] found that biomass chars produced during the rapid pyrolysis (in a drop tube reactor) were more reactive versus oxidation than chars produced in milder conditions (in thermogravimetric balance). In this study, two char samples were previously produced from both raw palm kernel shells (PKS) and torrefied PKS in an Isothermal Plug Flow Reactor (IPFR) under an almost oxygen-free atmosphere and a sufficient residence time, to guarantee the completion of the high temperature devolatilization. Finally, the char samples were tested in the IPFR by varying reactor temperature, oxygen concentration and residence time to study the biomass char oxidation behavior before and after torrefaction, and determine the char oxidation kinetics of torrefied biomass in combustion conditions that similar to those of full size power plants.

2. Fuel and methods

2.1. Fuel preparation

Two fuels are used in this work, PKS and torrefied biomass. PKS is the studied raw biomass material, abbreviated as RB. The torrefied biomass, abbreviated as TB, is the raw PKS torrefied at 300 °C for a residence time of 30 min in a horizontal rotary furnace. The proximate and ultimate analyses of those two biomass materials are summarized in Table 1. More detailed introduction of the torrefaction reactor and the studies on the biomass torrefaction tests can be found in previous work [11,14,15], where the yields of torrefied fuels and released gaseous species during torrefaction and the impacts of torrefaction on the biomass devolatilization performances and the biomass flame properties were well addressed. Continue to the previous studies, the char oxidation properties of the torrefied biomass will be characterized in this work and compared to that of raw biomass.

A sufficient amount of char is required to perform char combustion tests in the IPFR. In this work, char is produced in the IPFR at 900 °C under an almost oxygen-free atmosphere and a residence time of 300 ms. The proximate and ultimate data of the studied two chars are also listed in Table 1, the chars of RB-char and TB-char are collected after the designed devolatilization processes of RB and TB, respectively. It can be noted that the chars still contain a considerable amount of volatiles (about 16% and 21%), but this is significantly lower than their parent biomass fuels (about 50% and 70%). Similarly, the carbon content of biomass char increases and the oxygen content of biomass char decreases after torrefaction. Due to this study is to characterize the char oxidations, the heating