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

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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

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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 bio-masses
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

Table 1
Analysis of pulverized biomass.

	Proximate analysis, wt%					Ultimate analysis, wt%			
	MC^{ar}	VM^{db}	FC^{db}	Ash^{db}	LHV^{db} (MJ/kg)	C^{db}	H^{db}	O^{db}	N^{db}
RB	7.20	72.78	22.99	4.23	17.28	51.83	6.28	37.22	0.44
RB-char	/	21.44	62.18	16.38	/	53.60	2.25	27.17	0.60
TB	5.10	49.92	41.58	8.50	25.00	60.67	4.33	25.93	0.57
TB-char	/	16.27	68.59	15.14	/	67.54	2.53	14.17	0.62

values of RB-char and TB-char were not measured via standard calorific value tests, however, their high heating values of the chars can be easily estimated according to the proximate and ultimate data [16].

2.2. Isothermal Plug Flow Reactor

Char characterization tests were performed in the Isothermal Plug Flow Reactor (IPFR), a 4 m long drop tube furnace, which allows to characterize solid fuels under conditions similar to those of large power combustion plants, such as heating rates on the order of 10^4 °C/s, and a maximum temperature of 1400 °C. The scheme of the IPFR is shown in Fig. 1. The temperature of the tube is adjusted through eight electrically heated modules, and each of them can be controlled independently. A K-tron solid fuel feeder provides a continuous mass flow of about 100 g/h of pulverized fuel, which is fed to the reactor through one of the 19 available ports at different heights. The same ports can be used also to measure either the temperature of the flue gases or their chemical composition by using a gas sampling probe. The chemical composition of the oxidizer agent, injected into the IPFR reactor, can be adjusted by changing the flow rates of natural gas and air fed to the pre-combustor located on the top of the reactor. Once the velocity of the oxidizing gases is fixed, the desired residence time of biomass particles inside of the IPFR is achieved by changing the feeding port and the position of the sampling probe at the bottom of the reactor. The solid sampling probe consists of a water-cooled jacket where the collected particles are quenched with nitrogen in few milliseconds at a temperature below 300 °C to stop all the reactions. The qualification of the IPFR and the procedures applied to biomass characterization are presented by Biagini et al. [17], whereas the quantification of the experimental uncertainties (mass loss and residence time) was discussed by Li et al. [11].

In real biomass combustion systems, volatile combustion consumed a considerable part of the oxygen, resulting in the char oxidation occurs at a lower oxygen concentrations below 21%. In this work, the char oxidation tests are carried out by varying the oxygen concentration from 3% to 9%, and the residence time from 30 to 600 ms. A total of 20 tests were carried out under various conditions, as shown in Table 2.

During every char combustion test, the partially and/or completely burnt char particles are collected and then analyzed to determine the value of mass conversion according to the ash tracer
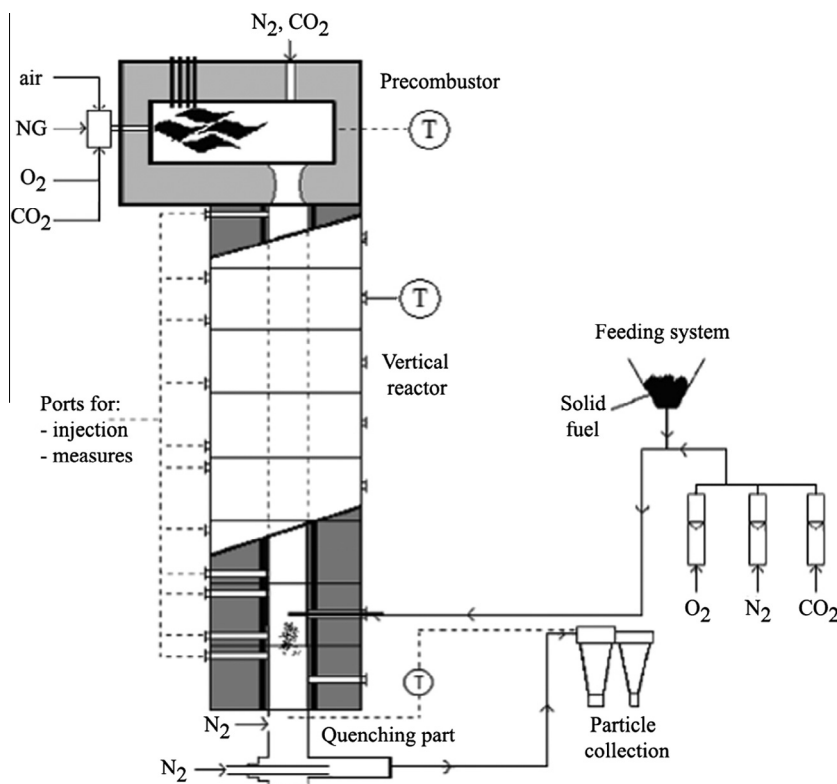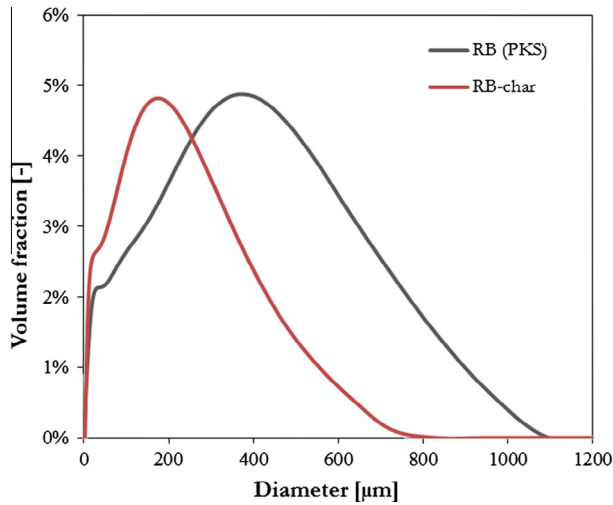

Fig. 1. Scheme of the Isothermal Plug Flow Reactor (IPFR).

Table 2
Resume of the char combustion tests performed in the IPFR.

Temp. (°C)	O$_2$ (vol.%)	Residence time (ms)						
		30	50	100	150	300	500	600
900	3	/	/	/	/	/	/	TB-char
900	4	RB-char	RB-char	/	RB-char	RB-char	RB-char	/
900	6	/	/	/	/	TB-char	/	TB-char
900	8	/	/	/	RB-char	RB-char	RB-char	/
900	9	/	/	TB-char	/	TB-char	/	TB-char
1200	4	RB-char	RB-char	RB-char	RB-char	RB-char	RB-char	/

Fig. 2. Particle size distributions of RB (PKS) and RB-char.

method, which assumes that the biomass ash is inert and thermally stable. Eq. (1) is used to determine the weight loss on a dry-ash-free basis.

$$X = 1 - \frac{ash_0}{ash} \cdot \left(\frac{1 - ash}{1 - ash_0} \right) \qquad (1)$$

A morphological analysis was also performed on the char samples. As an example, the particle size distribution of the produced RB-char was analyzed, and compared to that of its parent fuel, as shown in Fig. 2. It can be noted that produced char particle sizes are smaller than the parent ones, and the particle size distributions of chars produced from torrefied biomass and the parent material show a similar trend.

3. Kinetic determination approach

3.1. Char combustion model

The char combustion rate is controlled by the chemical kinetics and the external diffusion of oxygen. A uniform temperature inside of the particle is assumed due to its micro size. It is suitable to model the char combustion occurring under Regime II condition. The variation of particle mass is described by Eq. (2).

$$\frac{dm_p}{dt} = S_p D(P_{O_2,\infty} - P_{O_2,s}) = k(P_{O_2,s})^n \qquad (2)$$

The kinetic constant k is expressed in the Arrhenius form, whereas the oxygen diffusion coefficient varies with the temperature according to Eq. (3).

$$D = C \frac{\left(\frac{T_p + T_g}{2} \right)^{0.75}}{d_p} \qquad (3)$$

The temperature of the char particle is calculated from the heat balance of the particle. The particles are considered to be spherical, and the change of their diameter during char oxidation is also taken into account according to Eq. (4).

$$d_p = d_{p,0}(1 - X)^\alpha \qquad (4)$$

The burning mode is identified by the parameter α, which varies between 0 and 1/3, where $\alpha = 0$ corresponds to a constant particle size with decreasing density (Regime I), and $\alpha = 1/3$ corresponds to a decreasing particle size with constant density (Regime III). Since phenomena occurring during the latest stages of combustion are not considered in this study, i.e. char annealing and changes in particle structure, α is fixed at 0.25.

By manipulating Eq. (2), the unknown partial pressure of oxygen at the surface of the particle can be eliminated, and Eq. (5) is obtained.

$$\frac{dm_p}{dt} = S_p k \left(P_{O_2,\infty} - \frac{dm_p}{dt} \frac{1}{S_p D} \right)^n \qquad (5)$$

Analytical solutions can be found for apparent reaction order of 0.5 or 1, whereas in this study Eq. (5) is solved numerically.

It is important to highlight a few limitations of this model, which does not take into account phenomena occurring at high conversion levels, thus overestimating conversion for $X > 0.7$ [18]. Therefore, it is a "single film" model that does not consider secondary reactions occurring around the particle surface. For this reason CO is considered to be the only product of carbon oxidation, even if a not negligible amount of CO_2 should be formed. More detailed discussion on this model and its limitations can be found in [18].

3.2. Determination of apparent kinetics

The determination of the reaction order and the kinetic parameters follows the approach suggested by [19,20]. The apparent reaction order and kinetic parameters are determined by minimizing the root square mean error (RSME) between modeled and experimental conversions, described by Eq. (6), over a dataset of N experimental values.

$$RSME = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (X_{mod} - X_{exp})_i^2} \qquad (6)$$

A brute force method is employed to get the optimization parameters, constraining the activation energy to be between 10 and 200 kJ/mol and the pre-exponential factor to be positive. Finally, the joint optimization of the two parameters is repeated for reaction orders between 0.05 and 2.00. Char oxidation models are usually based on either apparent or intrinsic kinetics. The intrinsic approach considers the particle reaction rate as a function of the intrinsic reactivity, pore surface area, and local oxygen concentrations, whereas the apparent kinetics consider an overall reaction rate and the reaction rate is based on the external surface area and on oxygen concentration at particle surface [21]. The

evolution of the surface area of biomass is very complicated, in this work, the apparent activation energy is applied, considering the elementary char oxidation steps are lumped into a single one.

4. Results and discussions

4.1. High-temperature char oxidation tests

Char oxidation characterization, performed in semi-industrial facility-IPFR, leads to more reliable kinetic parameters than studies performed in traditional analyses, e.g. TGA. First of all, the char particles produced under high heating rate in the IPFR are more similar to those found in industrial furnaces. Then, their combustion rate is controlled by both the chemical kinetics of carbon oxidation and the diffusion of oxygen around the particle. In contrast, char oxidation tests performed in a TG balance usually occur under kinetically controlled Regime I conditions.

Fig. 3(a) shows the results of char oxidation tests performed on the raw PKS, at 900 °C with two oxygen concentrations (4%, 8%) and at 1200 °C with 4% oxygen. It is concluded that both oxygen diffusion and kinetics play an important role on biomass char oxidation at 900 °C, while at the elevated temperature of 1200 °C, the biomass char burns completely even at diluted oxygen concentration conditions within 500 ms. This result could further support

the volumetric combustion concept applied in large-scale boilers [22], which supposed to create a good complete combustion atmosphere at elevated temperature but diluted oxygen concentrations realized by internal recirculation of flue gas, achieving uniform temperature profile and gas species distributions. In fact, the difference between the char burnout profiles obtained at 900 °C with varying oxygen concentrations ($\approx$10%) is less relevant than the difference between the char burnout profiles obtained at varying temperature with constant 4% oxygen concentration ($\approx$30%). However, at 900 °C, a longer residence time is required to reach such a conversion level even at an enhanced oxygen concentration of 8%. Combustion tests of torrefied biomass char were performed as well. Fig. 3(b) shows the results of char oxidation tests performed at 900 °C with oxygen concentrations ranging from 3% to 9%, to understand the impact of torrefaction on the char oxidation process. A high oxygen concentration leads to an increase of mass conversion of the TB-char by 15% and 20% for 6% and 9% oxygen concentrations respectively.

When comparing the mass conversions of RB-char and TB-char oxidizations at 900 °C with varying oxygen concentrations, apparently, the mass conversion rate of RB-char is faster than the TB-char even oxidized at a lower oxygen concentration, for instance, 35.29% of TB-char is converted at 6% oxygen concentration compared to 40.79% of RB-char conversion at 4% oxygen concentration. In addition, Fig. 3(b) shows that the impact of torrefaction on char conversion is significant in the early-stage char oxidation process, while torrefaction shows less effect on the final mass conversions of char. Oxygen concentration has a considerable effect on the final mass conversion when operating at the same temperature. A similar result was reported from a TGA study on raw and torrefied biomass, aimed at studying their reactivity in air. In this TGA tests, the torrefaction process influences the parameters of the first stage, whereas those corresponding to the second remained unaffected [9]. This is desired, since torrefaction favors the formation of a stable flame during combustion in a pulverized-fuel burner. First, according to the previous work on biomass flame [14], biomass normally has a wider flame volumes when compared to that of coal, and the volume of biomass flame reduces after torrefaction and similar to coal flames, and therefore a combustion stability can be expected when co-firing torrefied biomass with coal. Additionally, this could be also explained as the change of cellulose structure during the torrefaction process because of the decomposition of hemicellulose, which further influences the char structure formed after high-temperature devolatilization, benefitting a stable combustion.

4.2. High-temperature char combustion kinetics

The kinetic parameters of char oxidation for the studied raw and torrefied biofuels, determined by minimizing the differences between modeled and experimental results, are finally presented in Table 3. It can be noted that the accuracy of the model prediction is acceptable, with a root square mean error of 4.50% and 8.60% for RB-char and TB-char, respectively.

Due to the TB-char oxidation tests were only performed at one temperature 900 °C, it was not possible to determine the appropriate activation energy, because particle temperatures will not differ in the different experimental runs. Here, the apparent activation
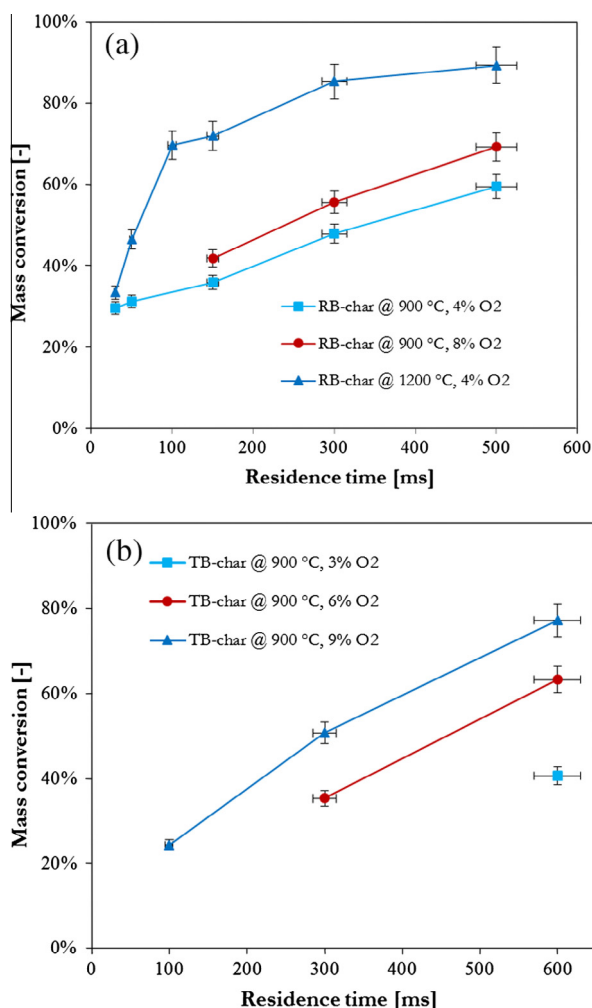

Fig. 3. Mass conversion during char oxidation tests at different oxygen concentrations ((a) RB-char; (b) TB-char).

Table 3
High temperature char combustion: kinetic parameters.

	A (kg/m^2 s Pa^n)	E (kJ/mol)	n (−)	RSME (−) (%)
RB-char	0.3900	47.5	0.29	4.50
TB-char	0.0037	60.0	0.80	8.60

energy for TB-char is chosen to be 60 kJ/mol, while the pre-exponential factor and reaction order are determined by same approach. In addition, the oxygen reaction order is significantly higher for TB-char than for RB-char, which agrees with the experimental data that show a more relevant contribution of oxygen to the overall conversion for the former than for the latter biomass char. Accordingly, it is impossible to compare the char reactivity of RB-char and TB-char by the activation energy only, but a good prediction can be expected by applying the determined kinetics.

The obtained kinetics of the studied chars are compared by Arrhenius plot with referenced biomass and coal kinetics, as shown in Fig. 4. The referenced biomass and coal kinetics are selected from literature [23], in which Karlström et al. studied anthracite chars and char from beech tree, their kinetics were obtained based on experiments at varying temperatures (950 °C, 1200 °C, and 1400 °C) and varying oxygen conditions (4%, 6%, 8%, and 12%). In Fig. 4, the O_2 concentration is fixed as 4% for comparison. It is clear that the reactivity of RB-char is high, and the reactivity of TB-char is comparable with the tree-char from Karlström's work, while the reactivity of all the biomass chars are significantly higher than that of anthracite char. The slope of the line in Arrhenius plots represents the activation energy, the selected activation energy for TB-char is in the similar ranges of referenced biomass char while still significant lower than that of anthracite char, this could be concluded that the chosen activation energy of 60 kJ/mol for TB-char is reasonable, and the predicted mass conversions of studied char oxidations based on the obtained all kinetic parameters will be examined and validated later.

4.3. Examination of determined kinetics

Fig. 5 shows the comparison between the predicted and the experimental mass conversion for char combustion of the raw (a) and torrefied (b) PKS, which demonstrates the ability of the model to predict the conversion trend with a sufficient degree of accuracy. The kinetic parameters of char oxidation of raw and torrefied PKS determined in this work are thus examined and validated. From Fig. 5(a), it can be concluded that, at the relatively low temperature of 900 °C, the mass conversions of RB-char are underpredicted in the early stage of char oxidation, while the final mass conversions are slightly over-predicted when compared to experimental data. When the temperature rises up to 1200 °C, a good
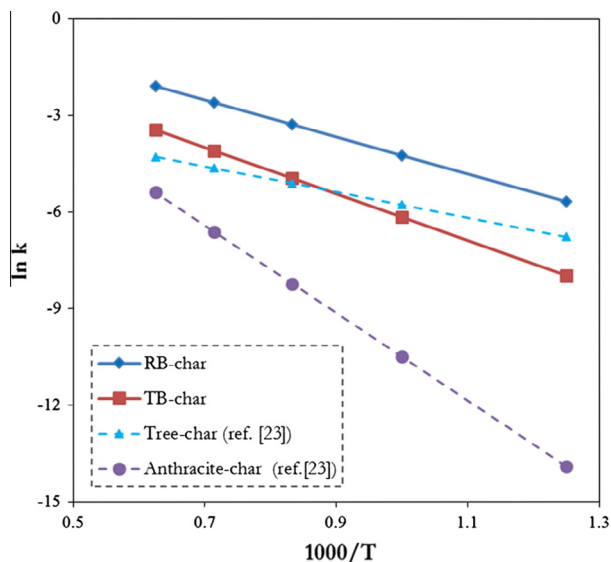

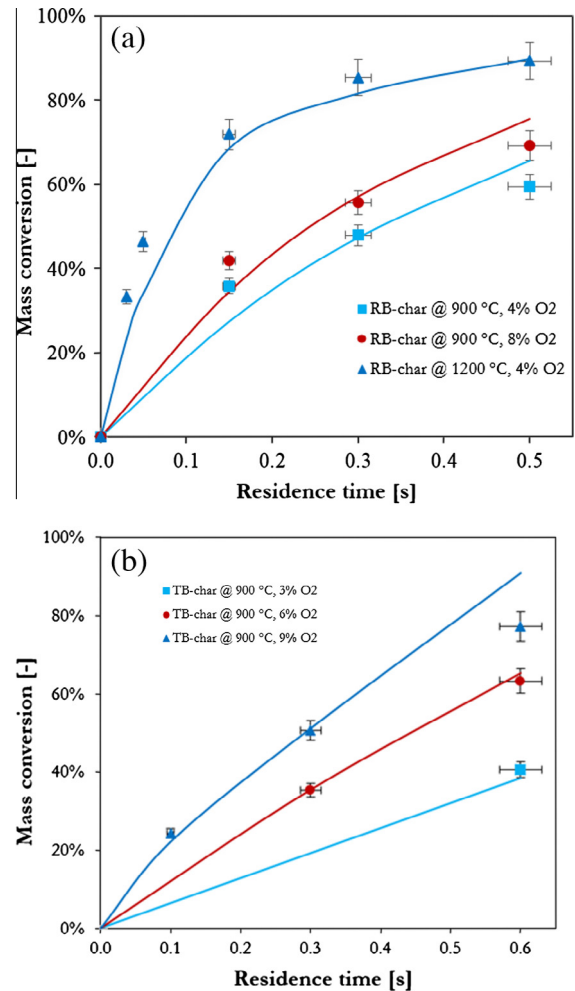**Fig. 4.** Arrhenius plots for studied RB-char and TB-char and compared with referenced chars.

Fig. 5. Comparison between modeled and measured mass conversions ((a) RB-char; (b) TB-char).

agreement is achieved, although the predicted mass conversion is in a small degree lower than the experimental data, and a good prediction for the final mass conversion is obtained. According to the char oxidation model, the oxidation rate is governed by both kinetic and oxygen diffusion. When the operating temperature reaches 1200 °C, the char is combusted under Regime III, in which reaction rate is dominantly controlled by diffusion.

Fig. 5(b) shows a similar mass conversion trend for TB-char, the mass conversions of TB-char are slightly under-predicted in the early stage of char oxidation, while the final mass conversions are over-predicted when compared to experimental data, and the predicted mass conversions show good agreements with experimental data. A big gap between experiments and prediction is shown in TB-char oxidized at 900 °C and 9% oxygen concentration case in late oxidation stage, this might be caused by the experimental errors, and the errors could be made experimentally either by uncertainties of mass loss or by uncertainties of residence time, the uncertainties caused by experiments have been comprehensively discussed in our previous work [11]. Another reason might be the small ash content when compared to the fixed carbon content in studied char samples, while the mass conversion during char oxidation is calculated based on the Eq. (1), a small uncertainty on the ash content measurement may cause a significant difference in mass conversion, however unfortunately, there is still lack an measurement method to accurately track the mass conversion of solid thermal conversions in plug flow reactor. In

general, it can be concluded the determined kinetics of RB-char and TB-char can be used to predict the mass conversions during the char oxidation processes.

5. Conclusions

The promising properties of torrefied biomass provide a co-utilization option to incorporate large percentage biomass co-firing ratio in existing coal-fired boilers without major modifications. Torrefied biomasses are supposed to be a coal-like fuel used in industrial furnaces. Torrefied biomass is expected to have a better combustion stability than raw biomass and similar to that of coal. In this work, the studied two chars were produced from both raw and torrefied biomass in conditions similar to real combustion systems, i.e., high temperature and heating rate. The char samples were then combusted in the IPFR reactor at varying temperature, oxygen concentration and residence time. According to the results, the char produced from torrefied biomass was less reactive than the one from raw biomass. The impact of torrefaction on char conversion was significant in the early-stage char oxidation process, while torrefaction showed no effect on the final mass conversion. Oxygen concentration gives a relevant contribution when the char is oxidized at the same temperature. Finally, the char oxidation kinetic parameters were determined using a parameter optimization method, which minimizes a least squares-based objective function of the difference between model and experimental results. The predicted mass conversion showed a good agreement with experimental data, especially at high temperatures.

Acknowledgements

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