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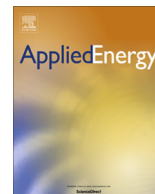
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Characterization of biomass combustion at high temperatures based on an upgraded single particle model



Jun Li ^{a,*}, Manosh C. Paul ^{a,*}, Paul L. Younger ^a, Ian Watson ^a, Mamdud Hossain ^b, Stephen Welch ^c

^a Systems, Power & Energy Research Division, School of Engineering, University of Glasgow, Glasgow G12 8QQ, UK

^b School of Engineering, Robert Gordon University, Aberdeen AB10 7JG, UK

^c BRE Centre for Fire Safety Engineering, School of Engineering, University of Edinburgh, Edinburgh EH9 3JL, UK

HIGHLIGHTS

- High temperature rapid biomass combustion is studied based on single particle model.
- Particle size changes in devolatilization and char oxidation models are addressed.
- Time scales of various thermal sub-processes are compared and discussed.
- Potential solutions are suggested to achieve better biomass co-firing performances.

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ABSTRACT

Biomass co-firing is becoming a promising solution to reduce CO₂ emissions, due to its renewability and carbon neutrality. Biomass normally has high moisture and volatile contents, complicating its combustion behavior, which is significantly different from that of coal. A computational fluid dynamics (CFD) combustion model of a single biomass particle is employed to study high-temperature rapid biomass combustion. The two-competing-rate model and kinetics/diffusion model are used to model biomass devolatilization reaction and char burnout process, respectively, in which the apparent kinetics used for those two models were from high temperatures and high heating rates tests. The particle size changes during the devolatilization and char burnout are also considered. The mass loss properties and temperature profile during the biomass devolatilization and combustion processes are predicted; and the time-scales of particle heating up, drying, devolatilization, and char burnout are compared and discussed. Finally, the results shed light on the effects of particle size on the combustion behavior of biomass particle.

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1. Introduction

Biomass is a sustainable fuel that can deliver a significant reduction in net carbon emissions when compared with fossil fuels, and environmental and social benefits could also be expected [1]. However, due to high volatile contents and low energy densities, the combustion properties of biomass are significantly different from those of coals, limiting the biomass substitution ratios in co-firing boilers. Currently, biomass co-firing levels are mostly below 5% on energy basis, while more than 10% biomass substitution are seldom commercialized [2,3]. An efficient biomass co-firing solution is therefore required to attain

large percentages of biomass co-firing in existing pulverized coal boilers.

When entering a pulverized-fuel flame, biomass particles are rapidly heated to a final temperature in the range of 1400–1600 °C at a rate of approximately 10⁴ °C/s [4,5]. However, most common analysis based on TGA is not able to determine the accurate kinetics of biomass combustion at real furnace conditions, due to the relatively low temperatures (<1000 °C) and low heating rate (<1 °C/s) [5]. Therefore, there is a clear lack of a suitable biomass combustion model with feasibility of representing more faithfully a true boiler or furnace condition, in which biomass particles are heated rapidly to high temperatures. Accordingly, the study of biomass thermal behavior at real combustion conditions is the first step in understanding biomass combustion behavior and possibility of large percentage co-firing with coals.

* Corresponding authors. Tel.: +44 (0)141 330 8466.

E-mail addresses: Jun.Li@glasgow.ac.uk (J. Li), Manosh.Paul@glasgow.ac.uk (M.C. Paul).

Nomenclature

Symbols

A	pre-exponential factor in Arrhenius expression (1/s)
C	carbon content (% dry ash free basis)
D	diffusion rate coefficient (m^2/s)
d_p	particle diameter (m)
E	activation energy (J/kmol)
f	fraction of heat absorbed by solid residuals
k	kinetic constant ($\text{kg}/\text{m}^2 \text{ Pa s}$)
$\dot{k}$	thermal conductivity ($\text{W}/\text{m K}$)
m	mass (kg)
MC	moisture content (%)
n	reaction order (–)
P	pressure (Pa)
r	particle radius (m)
R	gas universal constant $8.3143 \text{ J}/(\text{mol K})$
S	char specific surface (m^2/kg)
T	temperature (K)
X	mass conversion (–)
α	particle size evolution exponent (–)

Subscripts

B	biomass
$Char$	char
dry	drying
$devo$	devolatilization
exp	experimental
g	gas phase
M	moisture
mod	modeled
ox	char oxidation
p	particle
s	solid remains
$vola$	volatile
w	furnace wall
0	initial value

Biomass combustion has widely been studied based on a single particle model [6–18]. For example recently, Porteiro et al. [13] employed a single particle model to investigate the biomass thermal conversions, considering both intra-particle combustion and extra-particle transport processes to describe the thermal deration of biomass particles; the impacts of structure changes on the heat transfer properties of wood was also studied in their further work [12]. To study the combustion properties of a woody biomass particle, Haseli et al. [14] upgraded a one-dimensional particle model accounting for particle heating-up, devolatilization, char oxidation, and gaseous phase reactions. Lu et al. [15,16] reported the effects of particle size and particle shape on the devolatilization and combustion performance of biomass employing a one-dimensional particle model and discussed with their experimental results. Yang et al. [18] studied combustion characteristics of a wide range of sizes biomass (10 μm to 20 mm) using same single particle modeling approaches.

This paper studies biomass combustion properties at a high temperature and high heating rate that are similar to the conditions in a real furnace. A computational fluid dynamics (CFD) combustion model of a single biomass particle is employed, and the existing devolatilization and char oxidation models are upgraded to study high-temperature rapid biomass combustion behavior. Biomass devolatilization reaction rate and the amount of released volatiles are governed by a two-competing-rate model, considering the swelling properties of biomass particle during its devolatilization process. The biomass char oxidation rate is controlled by both kinetics and oxygen diffusion combining an empirical method for predicting particle size changes with char burnout. The mass loss properties and temperature profile during the biomass devolatilization; and combustion processes are predicted, and the timescales of particle heating up, drying, devolatilization, and char burnout are discussed.

2. Fuel and method

2.1. Fuel and kinetics

The studied woody biomass is palm kernel shell (PKS), and its proximate and ultimate properties are listed in Table 1. The apparent kinetics of devolatilization and char oxidation of biomass have

been previously determined by a series of tests in an isothermal plug flow reactor (IPFR) [4,5], as also presented in Table 1.

2.2. Modeling approach

This numerical study concerns exposing a woody biomass particle in a high temperature furnace; the oxidizing agent, air, comes from one side of the furnace, and the flue gas flows out from the other side. The whole combustion process includes the particle heating-up, drying, devolatilization, and char oxidation. Once exposed in the high temperature furnace, the biomass particle is heated up by the surrounding furnace wall and oxidizing agent via radiation and convection, resulting in a rise in the surface temperature of the biomass particle. The released heat is then transferred from the particle surface to its center by conduction. The moisture and volatile matter are released once the particle temperature has reached a reactive temperature, and the drying and devolatilization rates depend on the particle temperature.

The amount of released volatile matter depends on the fuel type and devolatilization conditions, and the volatiles mainly consist of gaseous hydrocarbons at high temperatures. However, due to the complexities in the chemical reactions, the kinetics of individual gaseous species released during the devolatilization are still not well understood. It is reasonable to represent the volatile matters by a single virtual material, although in practice it contains many kinds of species [19]. A surface reaction model is applied for the char oxidation process that takes place on the particle surface, while an empirical shrinking model is applied to simulate the particle size changes.

2.3. Mass and energy conservations

The equations presented below describe the evolution of solid components including dry biomass and char. Ash is not considered in this simulation due to its small amount.

$$\frac{\partial \rho_B}{\partial t} = -k_{devo} \rho_B \quad (1)$$

$$\frac{\partial \rho_{Char}}{\partial t} = (1 - v_{Vola}) k_{devo} \rho_B - k_{ox} \rho_{Char} \quad (2)$$

Table 1
Fuel properties and kinetics of studied biomass.

Proximate analysis (wt.%)				Ultimate analysis (wt.%)				LHV ^{db} (MJ/kg)
Moisture ^{ar}	Volatile ^{db}	FC ^{db}	Ash ^{db}	C ^{db}	H ^{db}	O ^{db}	N ^{db}	
7.20	72.78	22.99	4.23	51.83	6.28	37.03	0.44	17.28
Devolatilization kinetics [4]				Char oxidation kinetics [5]				
A ₁ (s ⁻¹)	A ₂ (s ⁻¹)	E ₁ (kJ/mol)	E ₂ (kJ/mol)	V ₁	V ₂	A _C (s ⁻¹)	E _C (kJ/mol)	n
602	8000	42.5	130	0.86	0.96	0.39	47.5	0.29

The moisture is considered separately as a liquid component, and when the local temperature reaches the vaporization temperature, the drying process starts and its rate is control by kinetics:

$$\frac{\partial m_M}{\partial t} = -k_{dry} m_M \quad (3)$$

The local moisture content is readily calculated with the following equation:

$$MC = \frac{\rho_M}{\rho_B + \rho_{Char} + \rho_M} \quad (4)$$

The conservation of energy for the solid phase accounting accumulation, conduction, radiation, and heat released from both homogeneous and heterogeneous reactions is shown in Eq. (5).

$$\begin{aligned} \frac{\partial T_p}{\partial t} (\rho_M C_{P(M)} + \rho_{DB} C_{P(DB)} + \rho_{Char} C_{P(Char)}) \\ = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 k' \frac{\partial T_p}{\partial r} \right) + \tilde{Q} \end{aligned} \quad (5)$$

2.4. Devolatilization

The yielded amount of high temperature volatile matter (HTVM) is commonly more than that of standard volatile matter [4]. Two-competing-rate model is employed to simulate the devolatilization and then predict the high temperature volatile matter yield [20], in which the first reaction (A_1 , E_1 , and α_1) is used to calculate the devolatilization rate at lower temperatures, while the second reaction (A_2 , E_2 , and α_2) plays a dominant role at higher temperatures. The two kinetic rates are weighted to yield an expression of weight loss during the devolatilization process:

$$\frac{m_v(t)}{m_{p,0}} = \int_0^t (\alpha_1 k_1 + \alpha_2 k_2) \exp \left(- \int_0^t (k_1 + k_2) dt \right) dt \quad (6)$$

where $m_v(t)$ is the volatile yield over time, and $m_{p,0}$ is the initial particle mass at injection. The kinetic rates are all expressed in Arrhenius form.

2.5. Swelling coefficient

Based on the fuel and char morphological analysis by comparing the average particle diameter of biomass before and after high-temperature devolatilization, the swelling coefficient was determined as 0.7, representing the biomass particle shrinkage during its devolatilization process. The diameter of a particle may change significantly during devolatilization based on its swelling coefficient is calculated from

$$\frac{d_p(t)}{d_{p,0}} = 1 + (C_{sw} - 1) \frac{(1 - f_{w,0})m_{p,0} - m_p}{f_{v,0}(1 - f_{w,0})m_{p,0}} \quad (7)$$

where the second term in the right hand side is the ratio of the mass that has been devolatilized to the total volatile mass of the particle.

2.6. Char oxidation

Models based on apparent kinetics have frequently been used to model char oxidation rates under conditions limited by the combined effects of chemical kinetics and diffusion. According to this model, the char oxidation rate can be predicted as [21]:

$$\frac{dm_p}{dt} = S_p k \left(P_{O_2, \infty} - \frac{dm_p}{dt} \frac{1}{S_p D} \right)^n \quad (8)$$

The evaluated diameter is modeled according to the following equation:

$$\frac{d_p}{d_{p,0}} = (1 - X)^\alpha \quad (9)$$

where d_p is the particle diameter (the subscript 0 indicates the initial value), and X is the degree of burnout. The limits of the burning mode are $0 \leq \alpha \leq \frac{1}{3}$, where $\alpha = 0$ refers to a constant particle size with a decreasing density and $\alpha = \frac{1}{3}$ corresponds to a decreasing particle size with a constant density throughout the conversion. It is also important to note that the burning mode of a function of particle size and combustion conditions. Due to the impacts of burning mode on the burnout prediction is mainly at late combustion stages, to the burning mode is fixed as 0.25 in this simulation [22].

3. Results and discussions

The models with the determined kinetic parameters used for high-temperature rapid devolatilization and char oxidation process have been validated in previous work, by comparing the predicted mass loss of studied biomasses with their corresponding experimental values at the varying temperatures [4,5].

Fig. 1 presents the general view of the total combustion of 1 mm spherical biomass particle, as well as the individual mass loss predictions of drying, devolatilization and char oxidation processes, which are known as the three main stages occurred during biomass combustion. The drying process terminates quickly less than 1 s compared to about 3 s for the completion of devolatilization. It is also noticed that the char production increases gradually with the volatile release and reaches a peak after the completion of the volatile matter release, then the char oxidation starts immediately and continues until the produced char is consumed completely in approximately 7 s. In addition, Fig. 1 clearly shows that, after drying and devolatilization, the char oxidation curve overlaps the total biomass combustion curve, because the solid remain is char and ash is not considered in the total mass weight in this simulation.

3.1. Heating up of biomass particle

After being exposed to a high temperature combustion furnace, biomass particle is heated up quickly by both radiation and convection heat transfer. The biomass surface temperature could be easily calculated according to the total heat flux onto the biomass

particle. The surface temperature of biomass particle is important to the biomass combustion, which determines the total heat flux conducting from the particle surface into particle center, and thus finally governs the drying and devolatilization processes along the biomass particle radius.

The effects of particle size and furnace temperature on the biomass surface temperature have been investigated in this work. Fig. 2a shows that the particle of 1 mm could be heated up to the furnace temperature much faster than a 10 mm size biomass particle. Thus, it could be concluded that the heating up process becomes more important for larger size biomass particles, because it requires more time to be heated up which subsequently slows down the combustion process.

Fig. 2b compares the heating history of the two different sizes of particle (1 mm and 4 mm) exposed into the combustion chamber at two different temperatures (700 °C and 900 °C). It can be observed that a higher temperature accelerates the heating up process for studied two particles, especially for larger size particles.

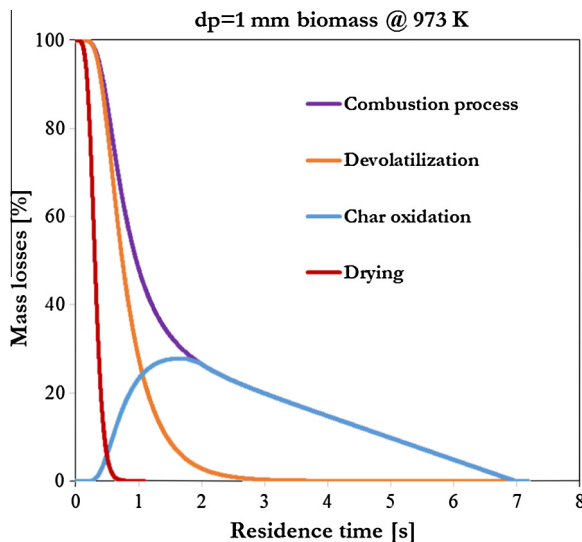
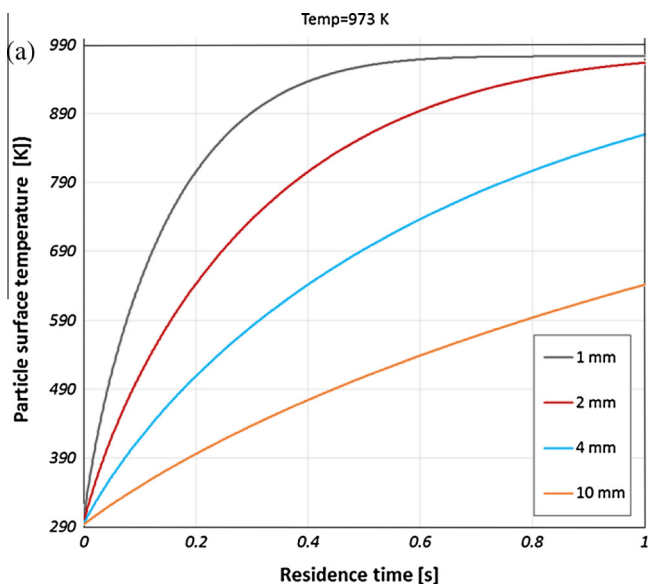


Fig. 1. Mass loss curves in biomass particle combustion.



3.2. Drying process

The moisture is considered, in this work, separately as a liquid component, and when the local temperature reaches the vaporization temperature, the drying process starts and its mass loss rate is governed by kinetics. Fig. 3a shows that larger biomass particle requires more time to complete the drying process at a fixed furnace temperature, for example, 1 mm biomass particle is dried completely in less than 1 s, while a 10 mm biomass particle requires 2.5 s in its drying process when both of them are exposed into a 700 °C furnace. Thus the drying process requires more residence time in drying for larger biomass particles. Fig. 3b compares two different sizes particle (1 mm and 4 mm) exposed into combustion chamber at temperatures of 700 °C and 900 °C. It is clearly observed that an elevated temperature significantly accelerates the biomass particle drying process for both particles.

3.3. Devolatilization process

The volatile matter yielded at high temperature is higher than the standard volatile matter revealed by proximate analysis. An accurate prediction of the volatile matter yield with temperature is thus important for chosen combustion model. In the previous work [4], high-temperature rapid devolatilization tests of pulverized biomass samples were carried out in the IPFR reactor to determine realistic devolatilization kinetics based on a two-competing-step model. The determined kinetics are employed to simulate devolatilization and predict the HTVM yields in this work. Fig. 4a shows that, larger biomass particle requires more time to complete the devolatilization process, for instance, 1 mm biomass is dried completely in 3 s, while a 10 mm biomass particle requires more than 5 s to complete its devolatilization process when they are placed into a 700 °C combustion chamber. Fig. 4b compares two different sizes particle (1 mm and 4 mm) exposed into the combustion chamber at different temperatures of 700 °C and 900 °C, and it is clearly observed that the higher temperature favors the biomass particle devolatilization process for both particles. In addition, when increasing the furnace temperature from 700 to 900 °C, the devolatilization rate of the 4 mm biomass particle shows a greater acceleration than that of the 1 mm biomass particle.

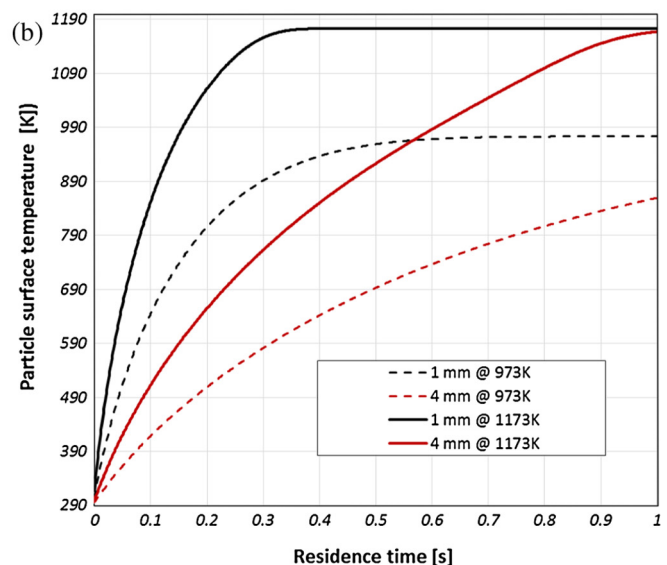


Fig. 2. Effects of particle size and furnace temperature on the particle heating up.

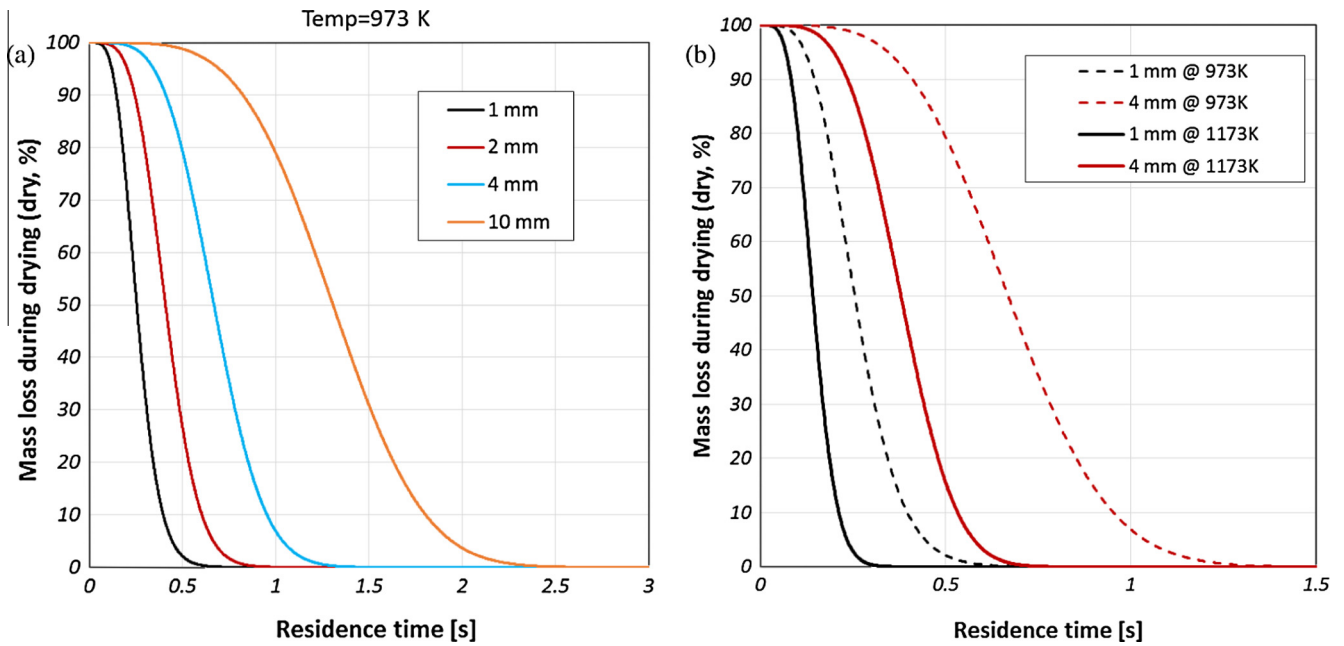


Fig. 3. Effects of particle size and furnace temperature on the drying rate.

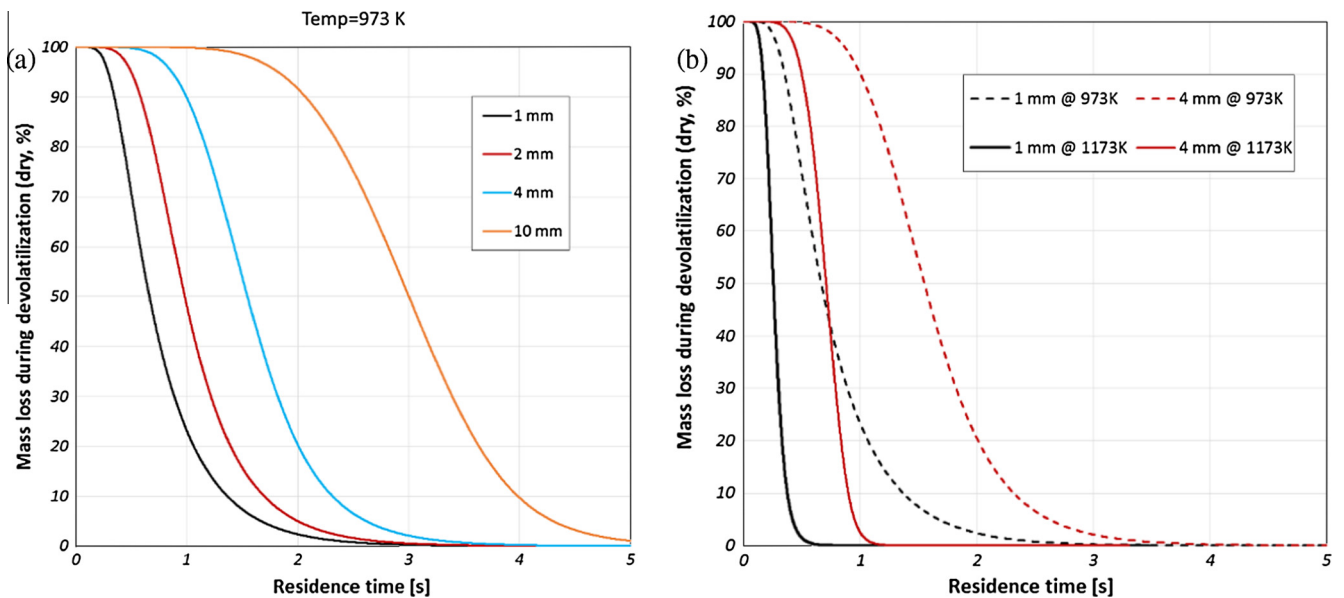


Fig. 4. Effects of particle size and furnace temperature on the devolatilization rate.

3.4. Char oxidation process

In the combustion process of woody biomass, the rate of char oxidation is typically slow [23]. As evidenced in Fig. 1, the completion of char oxidation requires more residence time than the drying and devolatilization processes, and thus the rate of char oxidation determines the overall combustion progress. In the previous study [5], the reactivity of biomass chars were analyzed in IPFR reactor, and the char oxidation kinetic parameters based on a kinetic/diffusion model were determined using a parametric optimization method. Fig. 5 shows that the char oxidation rate of the smaller size biomass particle is higher than that of the larger one. Similar to drying and devolatilization, an elevated temperature also significantly accelerates the char burnout process.

3.5. Timescales comparison of studied thermal processes

The timescales for the energy conservation inside the particle, the internal heat transfer, the chemical decomposition, and the external heat transfer at the surface are commonly characterized to recognize the importance of individual thermal process [24]. Table 2 compared the required residence time for heating the biomass particle surface temperature to furnace temperature, which is 973 K in this case; the residence time for moisture remain less than 0.01% during the drying process; the residence time for the volatile releasing over 99.99%; and the residence time for over 99% char consumption for the 4 different biomass particles combusting with air at 973 K. Obviously, the drying process is completed before the biomass particle reaches to furnace temperature, expect the 1 mm biomass particle, this might be the radiation heat

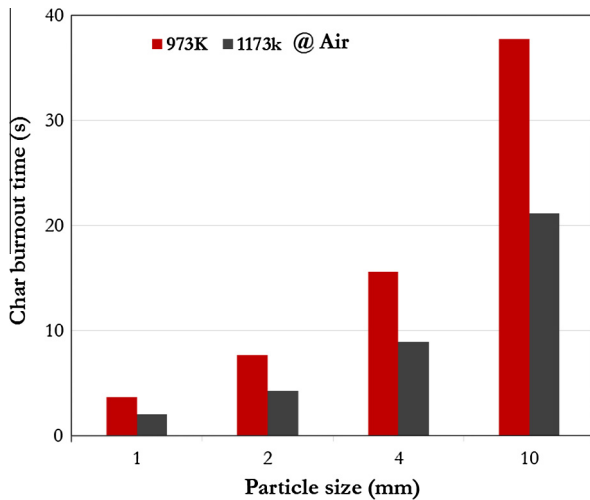


Fig. 5. Effects of particle size and furnace temperature on the char oxidation rate.

Table 2

Residence time required to complete thermal processes at 973 K and air condition.

Biomass particle sizes	Required residence time (s)			
	Heating the particle surface temp. to 973 K	Drying (wt.% < 0.01%)	Devolatilization (wt.% < 0.01%)	Char oxidation (wt.% < 1%)
1 mm	0.733	0.817	4.405	5.07
2 mm	1.274	1.081	4.736	7.66
4 mm	2.174	1.557	5.351	15.59
10 mm	4.558	2.749	7.043	37.77
$\frac{\Delta\tau}{\Delta d_p}$	0.463	0.234	0.307	3.417

flux get through the particle center quickly for very small particle, while the drying process governed by kinetics could not be completed. The volatile matters releasing and char oxidation are still ongoing after the particle reached to furnace temperature. Compared to other studied thermal processes, the char oxidation requires a longest residence time, meaning that the char oxidation is the determined step in biomass combustion. This tendency is observed more clearly for larger particles combustion.

Furthermore, the larger the biomass particle, the greater the ratio of the char oxidation and devolatilization time is. When considering a co-firing purpose of biomass with coal blend, a larger size biomass particle would be expected to have a similar flame to that of pulverized coal particles, because coal typically contains less volatile but rich in char, and therefore a larger ratio of the char oxidation time and devolatilization time is also formed. Accordingly, once a similar flame profile in co-firing cases is obtained, the impacts on the heat exchangers surfaces, i.e. over/under heat load, inside a coal-fired boiler could be avoided.

Additionally, an average ratio of time difference over particle size difference, $\frac{\Delta\tau}{\Delta d_p}$, is employed to discuss the increases of required time for various thermal process, which is defined as:

$$\frac{\Delta\tau}{\Delta d_p} = \sum_{\substack{i,j=1,2,4,10 \text{ mm} \\ i \neq j}} \frac{\tau_i - \tau_j}{d_{p,i} - d_{p,j}} \quad (10)$$

where τ is the characterize time for varying thermal process, including heating, drying, devolatilization and char oxidation; d_p is particle diameter; subscripts i, j represent the different particle sizes (1, 2, 4, 10 mm).

The calculated results of the average ratio of time difference over particle size difference are listed in Table 2. When increasing the particle diameter by 1 mm, the residence time requires 0.463 s,

0.243 s, 0.307 s, and 3.417 s more to compete the studied thermal processes of heating, drying, devolatilization, and char oxidation respectively at furnace temperature of 973 K and air combustions. It could be concluded that the particle size shows less impacts on drying process, followed by devolatilization, heating, and char oxidation. This can be easily explained as the drying process is started at relative low temperature (105 °C), which could be completed before finishing the other thermal processes. Similarly, the volatile matter releasing normally starts when particle temperature is over approximate 300 °C and may keep releasing process through and/or after the entire heating up process, depending on the fuel types and final temperature. It is reported that the volatile matter yielded at high temperature is higher than the standard volatile matter revealed by proximate analysis, and thus an extended amount of volatile could be yielded, which requires an extra time. Char oxidation, controlled by both kinetics and oxygen diffusions, is a relative slow heterogeneous reaction at solid surface. And therefore, the char oxidation process is most sensitive to the particle size, an extra 3.417 s is needed for a 1 mm large in diameter biomass particle.

4. Conclusion

Biomass combustion properties at high temperatures have been characterized based on a upgraded single particle model in this work. The biomass devolatilization reaction was simulated by a two-competing-rate model and the biomass char burnout rate was controlled by both the kinetics and diffusion to predict the particle size changes. The results showed the char oxidation process required a longer residence time compared to the heating up, drying and devolatilization. In addition, an elevated temperature significantly enhanced all the processes occurring in biomass combustion. Moreover, it is concluded that the particle size shows most significant impacts on char oxidation, followed by heating and devolatilization, while less impacts of particle size is noticed on drying process. With an aim to potentially co-fire blend fuels, a relative larger biomass particle is expected to have a flame property similar to that of pulverized coal particles.

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